

SOAL-ORE PROCESSING OF CONTINUOUS
MULTI-FIBERS

By

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DEDICATION

I dedicate this dissertation to my parents.
Their love, support and wisdom have been and always
will be a constant source of strength and inspiration.

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*Abstract of Dissertation Presented to the Graduate School
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AC-DEL PROCESSING OF CONTINUOUS MILLEITE FIBERS

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There is an increasing demand for materials that can withstand high temperatures without a deterioration in mechanical properties. Incorporation of fibers in metal or ceramic matrices can produce composites that can maintain their strength at high operating temperatures. Kevlar fibers are a good candidate for such applications. Continuous fibers are a better choice for load bearing applications, as they provide higher strength than short fibers. Achieving continuous spinability and producing glass free millette fibers presented a challenge to researchers in the past.

The goal of this study was to determine the parameters necessary to produce a glass-free fibers with the ability to achieve continuous spinability. To accomplish this goal, several experiments were conducted. The rheological conditions for continuous spinability and the different factors that control the rheological behavior of the mol were determined. The optimum value for shearing agent/biomass

production under stress was determined. The effect of chelating agent on anionic transformation was investigated. Also, the role of aging and aging temperature in the processing of anionic films was determined. The effect of the chelating agent on the dissolution behavior and the purity of the final product was determined. The grain growth of anionic films was also studied.

It was shown that film aging was critical in achieving good-quality films. It was also shown that anionic transformation was enhanced with increasing aging time, and it was shown that film grain size decreases with the increase of aging temperature. Also, shorter aging times were required at higher temperatures.

Crystallographic determination showed anionic was the only phase present. It was shown that no detectable amounts of inorganic glass phase were observed in the films prepared in this study. In contrast, commercial films showed the presence of large inorganic glass phase. It was shown that the activation energy for grain growth was high. Grain growth was not significant for temperatures up to 1350°C for long annealing times (22 hours) or up to 1450°C for short annealing times (1 hour).

CHAPTER 1 INTRODUCTION

The demand for materials that sustain high temperatures (in excess of 1200°C) is increasing progressively. Many high-tech industries, particularly the aerospace industry, have numerous applications for such materials. Ceramic fiber composites have a major role in the manufacturing of components for high strength, high-temperature applications. A candidate material for ceramic fibers is mullite. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is a crystalline ceramic that has an orthorhombic structure and with an alumina/silica molar ratio of 3/2. Mullite has excellent creep resistance and strength retention at high temperatures [1,2]. In addition, mullite has good thermal shock resistance and chemical stability.

Sol-gel processing has been used in the production of mullite fibers due to the unique properties made available by using this technique. The sol-gel method permits precise control of properties and microstructure before and after heat treatment. By using this technique, fiber spinning can be accomplished at room temperature. Also, sol-gel processing provides better purity and control over homogeneity when compared to more conventional techniques.

The emphasis of this study was the production of continuous fibers. Continuous fibers are of special interest in heat treating structural composites.

Continuous fiber composites are generally stronger than short fiber composites when a load is applied in the direction parallel to fiber orientation.

The two primary challenges facing researchers in this area, were achieving continuous spinnability and producing fibers without a glass phase. Researchers have been able to produce fully crystalline molten fibers but were unable to achieve continuous spinnability [Yano03]. Commercially available molten fibers are currently prepared with horns [Bowdell]. This results in the presence of a glass phase. A glass phase can cause a microscopic discontinuity in the mechanical properties of the fiber at high temperatures.

In this study, several experiments were conducted to determine the factors that have an effect on melt-spun processing of molten fibers. The role of pre-spinning hydrolysis on the properties of fibers in the green state was studied. In addition, the effect of pre-spinning hydrolysis on the final microstructure of fibers was investigated. The conditions for continuous spinnability for molten sol was also investigated. The various factors that contribute to achieving continuous spinnability and the factors that determine the rheological behavior of the molten sol were determined. The effect of chelating agents on organosol removal, molten transformations, and fiber microstructure was studied. The effect of varying the chelating agent/solvent precursor molar ratio on the sol rheology, sol molding, and fiber microstructure was also investigated.

Ageing of molten green fibers in humid air at different temperatures was studied. The effect of ageing on the properties and the microstructure of fibers was

determined. The role of aging on matrix formation was also investigated. In addition, the role of aging temperature on fiber microstructure and properties, and the advantages of high temperature aging were determined. Also the denaturation behavior of aged fibers was determined.

The presence of an isograftable glass phase was investigated. A comparison between the commercial fibers and the fibers produced in this study was carried out to determine if there were differences in the isograftable glass phase content. The final study was on grade growth of matrix fibers. Grade growth as a function of time and temperature was determined.

Statement of Problem

To investigate the critical factors and their underlying mechanisms in the fabrication of single phase matrix fibers by a method of continuous spinning.

Objectives

The objectives of this study were as follows:

- 1- Determine the conditions for continuous spinning for matrix sol and study the different factors that affect the rheology of the sol
- 2- Determine the effect of pre-spinning hydrolysis on fiber properties and microstructure,
- 3- Study the effect of chelating agent on organosol removal, matrix formation, and fiber microstructure.

- 6- Determine the optimum dissolving agent/solvent system used
- 7- Determine the effect of aging on matrix transformation. In addition, study the effect of aging on fiber microstructure and properties.
- 8- Investigate the effect of aging temperature on the properties and microstructure of fibers
- 9- Determine the densification behavior of fibers.
- 10- Determine the factors critical to single phase formation and retention after spinning.
- 11- Determine if the fibers produced contain an intergranular glass phase and compare the results to those for commercial fibers.
- 12- Study grain growth as a function of time and temperature

CHAPTER 1 LITERATURE SURVEY

Malinin Processing Via Sol-Gel

This study addresses the fabrication of malinin fibers using a sol-gel-based approach. Sol-gel processing was selected because of its unique characteristics which include excellent homogeneity, high purity, and low preparation temperatures [Mac02]. Large shrinkage, residual carbon (from sol components), and expensive raw materials are the main disadvantages. Malinin can be prepared using sol-gel from either single phase or diphasic gels.

Diphasic Gels

Gels that consist two different phases are often called diphasic gels. Malinin formation in diphasic gels involves a diffusion controlled growth mechanism by which the diffusion of the Al_2O_3 and SiO_2 components across the reaction layer controls the reaction rate [JLF04]. Aluminum species near the dissolving particle surfaces diffuse along the malinin/silica interface and react with the nearest available silicon species [Wu00a]. Silica species may diffuse in the opposite direction toward aluminum species. Malinin crystals form on the interface and grow toward the diphasic region. The growth rate of the interface is limited by a short-range transportation rate and the amount of the reactants. The malinin formation

temperature for this type of gels is high, about 125°C, compared to other approaches.

Diphenic gels were prepared by Prochaska and Klug [Pro45]. The aluminum precursor was aluminum isopropoxide, and the silica precursor was triphenylsiloxane. Both precursors were dissolved separately in cyclohexane. Equivalent volumes of the solutions corresponding to the desired alumina-silica composition were measured and mixed in a blender. Fifty-five grams of water per mol of each silicate was mixed with twice its volume of chloroform and added to the cyclohexane solution. The resulting sol was agitated then again for 24 hr. The solvent was evaporated at room temperature, and the residue was dried at 125°C. The resulting powder was calcined at 750°C.

The amount of residual carbon was observed to decrease with increasing heating rate. The alumina-silicates prepared by this method were amorphous up to 550°C where the formation of a crystalline phase was observed. The crystalline phase was determined to be either γ -alumina or α - Al_2O_3 upon XRD formation was detected at 1100°C.

Proh, Bolten and co-workers used metal silicates to make diphenic sol-gels [Pro47]. The silica sol was made by hydrolysis and polycondensation of $\text{Al}(\text{OC}_2\text{H}_5)_3$ (aluminum-*tert*-butoxide) followed by a peptization step. The resultant sol was a clear aqueous sol which contained $\text{Al}(\text{OH})_3$ colloidal particles. These particles were reacted with $\text{Si}(\text{OC}_2\text{H}_5)_4$ (tetraethyl orthosilicate) in a water-ethanol medium forming a chemically-bonded silica layer around and in between the

particles. Crystallization occurred after a short period of time yielding transparent particles about 1 μm in size upon drying at 500°C for 30 min.

Differential thermal analysis (DTA) study showed a shallow endothermic peak between $400^\circ\text{C} - 1000^\circ\text{C}$ which was caused by the gradual loss of hydroxyl groups. Broad diffraction peaks for opal were observed using x-ray diffraction analysis (XRD) in a sample heated to 1000°C . A multiple literature exothermic differential thermal analysis (DTA) peak was observed at 1267°C . Upon heating to 750°C , the grains had a prismatic shape and a glass phase was present, predominantly at the triple junctions.

Mullite was also prepared from a diphasic gel by Ismail et al. [2007]. A boehmite sol was prepared using $\gamma\text{-Al}_2\text{O}_3$, while the silica sol was prepared using colloidal SiO_2 . The mixture of the two sols was gelled at a pH of 3. The gelation rate was controlled by the addition of hydrofluoric acid (HF). Larger additions of HF resulted in heterogelation [2007]. The dried gel was ground in an alumina-lined ball mill and calcined at 1400°C . The mullite formed was surface etched using dilute acids. The DTA showed the crystallization of mullite at temperatures above 1200°C . The grain composition of mullite powder were homogeneously present as a mixture of 50:50% and sintered at a temperature of 1650°C . Transmission electron microscopy (TEM) micrographs for sintered boehmite showed traces of a glass phase but no glass particles at triple points.

Aluminosilicate gels with $\text{Al}_2\text{O}_3/\text{SiO}_2$ composition ratio = 1, 1.5, and 2 were prepared by Wu and Hellman [2010a]. The precursors used were colloidal

para-titanate ($\text{AlO}(\text{OH})$) and variously crystalline (TiO_2). The TiO_2 , silica, and water with $\text{OH}(\text{H}^+ \text{HCl})$ were mixed together in a ratio of 50 wt% : 30 wt% : 20 wt%. After the mixture was aged in a 50°C bath for 3 hr, the colloidal para-titanate sol was introduced, and mixed for 30 min. The mixture was then aged in a 50°C water bath. After 24 hr, the mixture formed a translucent white gel.

It was observed that the two distinct phases, para-titanate, and amorphous silica, transformed independently up to 1200°C, then reacted in situ making closely related for formation of a precursor (amorphous or quasi phase)-silica was formed via nucleation and growth of single crystal grains by a process that was either reaction or short range diffusion controlled [Wick]. It was found that the growth rate was time-dependent. The origin of the time-dependent character of the growth rate was not explained. It was also shown that Al_2O_3 particles that were larger than 30 nm did not react completely with SiO_2 , particularly at low temperatures. These alumina particles appeared to be entrapped in the silica phase. Although the overall composition was stoichiometric, the transformation product was a silica-rich matrix phase with residual alumina particles.

Kushman and Alary attempted to explain the time dependence of the growth rate found in the Wu and Mahajan results [1983]. They argued that the growth rate of the matrix grains was controlled by the dissolution of alumina particles into the amorphous phase. When considering transport of alumina particles by the growing matrix grains, the number of transitional alumina grains

existing in the β -phase region decreases slowly with time. Consequently, the total rate of aluminum dissolution into the amorphous phase was not constant, but decreased slowly with time. This resulted in the time-dependent growth rate for molten grains.

Molten α -phase grains were also prepared by two methods [Good]. Two processing methods were investigated. In both methods, the molten α -al was prepared by dispersing milligrams of TEOS into an aluminum monohydride (AlH_3) sol. The aluminum monohydride sol was prepared by dispersing boronine powder in an aqueous solution using 0.07 and 0.03 per mol of aluminum monohydride. In the first method, the sol mixture was stirred in the acidic condition until gelation was completed. In the second method, gelation was performed by the addition of a few drops of 0.1 M NH_4OH into the acidic aluminum monohydride - TEOS sol. Both agglomerates in large as 25 to 30 μm were formed spontaneously.

Differential thermal analysis (DTA) analysis results showed that molten formation occurs at a relatively high temperature (1280°C). The XRD analysis showed the presence of an amorphous phase and a small phase below the 1280°C analysis. The high molten formation temperature enabled electrocrystallization to occur at temperatures as high as 1250°C. As a result, high crystallization rates were achieved. Upon heating at 1250°C, 99% of theoretical density was achieved in the first method, while a solute pressure of 441 MPa was needed to achieve the same density in the second method. The XRD pattern for samples from the first method showed the presence of a glass phase and a small phase together with molten after

heating at 1050°C. No glass phase was detected in samples treated similarly from the usual method.

A technique similar to the one developed by Sengupta¹ was used by Li and Thompson (J₁16). The dihydrate gel was prepared by dispersing boehmite powder in a dilute HNO₃ solution. A suitable amount of TEOS together with an equal volume of ethanol were added with the boehmite dispersion to give the stoichiometric ratio of chlorination reaction. Gelation was accomplished in 24 hr inside a 50°C oven. Dynamic x-ray diffraction (DXRD) results showed that the silica phase in the dihydrate gel remained amorphous throughout the heating process until it reacts with alumina to form mullite at 1250°C. The boehmite gel experienced the following transformation:



Li and Thompson showed that mullite formation followed an Avrami type, diffusion-controlled growth mechanism with the nucleation process was complete before substantial growth took place. Samples fired at 1300°C showed rod-like crystals.

Several dihydrate mullite gels were studied by Nave and Langhaar (Nave15). The mullite rods were prepared by calcining mullite gel at 1450°C for 2 hr. The mullite gel was prepared by peptizing pseudobrookite and colloidal silica and getting the sol very acidic. A 20-wt-% aqueous dispersion of calcined mullite powder was ball-milled and centrifuged to yield an approximately 50% suspension of fine rod particles.

Soaked sols were produced by introducing different amounts of the seed suspension to the molten sol before preparation was started. The sol was then gelled and dried at 10°C. The microstructure of the soaked gel was compared to the microstructure of the soaked gel after firing at 1200°C. Most gels were similar to the case of unsoaked gel, while gels soaked with 4 wt% molten seed showed equiaxed grains. No evidence of intergranular glass phase was found in the case of soaked gels.

A molten seed mixture of 8 D3 with grain different results. Grains grew into smaller grains having aspect ratios as high as 12:1. The rest of the sample was a matrix of fine, nearly equiaxed grains with some intergranular porosity. The large grains resembled whiskers in a fine-grained matrix. It was not confirmed if the presence of the elongated fibers reinforced the material.

The effect of precursor composition on molten formation and the resulting structure was investigated by Li and Thomson [Li75]. Diphasic gels with Al_2O_3 molar ratios of $4/1$, $3\frac{1}{2}/1$, $3/1$, $2/1$, and $1/1$ were used. Molten formation was initiated at about 1200°C for all samples with only slight differences in temperatures. The molten formation temperature was a minimum for an Al_2O_3 ratio of $3\frac{1}{2}/1$ and increased as the Al_2O_3 ratio of the gels increased or decreased. In the case of $4/1$ gel, dissolution of alumina into the molten solid solution was observed after the initial molten formation. The dissolution was reversed above 1450°C with the formation of $8-Al_2O_3$ and then a Al_2O_3 . A change of microstructure from equiaxed

to elongated rodlike grain structure was observed within a narrow range of compositions near the Al_2Si ratio of 3/1.

Li and Thomas developed another process to produce diphase gels. The silica sol was prepared by hydrolyzing TEOS in water and a silicic acid solution with a pH of 11 [Li94a]. After hydrolysis was completed, aluminum nitrate was introduced. The solution was gelled in a sealed container at 60°C for 1 day. Melting formation of the gel was detected above 1200°C. A 500°C peak observed in the DTA curve was attributed to the formation of Al-Si mixed amorphous oxides.

Single-Phase Gels

Gels that have molecular-scale mixing of the components are referred to as single phase gels. For silica, single phase gels have molecular-scale mixing of aluminum and silica through either coprecipitation of aluminum and silica salts or hydrolysis of mixed aluminosilicates [L94a]. Melting formation exhibits a nucleation-controlled mechanism. The melting transformation temperature for single phase gels is below 1000°C.

One of the major obstacles to making homogeneous single phase (polymorphic) silica gel is the significant difference in the hydrolysis and self-condensation rates of aluminum and silicon alkoxides. Silicon alkoxide hydrolyzes at a much slower rate than aluminum alkoxide [T94a]. Inhomogeneity arises from the formation of macromolecules that do not have silica stoichiometry.

A process was developed by Yoldis and Furrow to circumvent the hydrolysis rate difference problem [Yol44]. The silicon alkoxide was partially hydrolyzed while the aluminum alkoxide was not hydrolyzed. Upon the addition of the aluminum alkoxide to the silicon sol, a white precipitate formed, but this precipitate dissolved forming a clear solution within hours at 50°C. The final hydrolysis was carried-out either in the liquid state by adding water, which resulted in the formation of a gel or fine powder, or in the solid state when the sol was used like coatings or the deposition of thin films.

Mullite formation was observed to occur at 550°C in DTA measurements. Also, a large spontaneous densification occurred at 750°C. The low sintering formation temperature was attributed to the intimacy and homogeneity of aluminum-silicon bonding. The microstructure consisted of equiaxed mullite grains about 1-4 microns in size, with no evidence of a secondary amorphous phase [Fur67].

Iyer¹ and Tabor developed a process to produce sparsely aluminum-silicon sols [Iya63]. The process consisted of two hydrolysis steps. In the first hydrolysis step, aluminum isopropoxide monomer, acid solution was mixed with isopropyl alcohol, water and hydrochloric acid in a ratio of 1:1:1:1. To prevent the formation of precipitates, half of the alcohol was used to dilute the metal alkoxide, while the other half was mixed with the water and acid which was then slowly added to the alkoxide mixture. Tetraethoxysilane, isopropyl alcohol, water, and hydrochloric acid in the molar ratio of 1:3:10:1 were added separately to the aluminum sol in the second hydrolysis step.

After allowing the sol to gel in air, opacidity was noticed. The gel was dried at 105°C after being dried at 100°C. Analysis via XRD showed that mullite was the only phase formed. The microstructure of the dried material and the presence of glass phase were not discussed in this study.

Li and Thomson also developed a process to produce single phase mullite gels [Li90]. The aluminum precursor, $Al(OC_2H_5)_3/H_2O$, was dissolved in absolute ethanol. The solution was mixed with tetramethyl orthosilicate. The mixture was then gelled at a 40°C oven over a period of two weeks.

Dynamical x-ray diffraction (DXRD) results showed that the gel was completely amorphous up to approximately 1000°C, where mullite began to form. Mullite was the only crystalline phase detected, and the formation of a cubic spinel phase was not observed. Fourier transforms followed FT-IR analysis showed that at 550°C the gel has a mixture of amorphous silica and alumina, and at 950°C Al-O-Si bond formation was observed. Transmission electron microscopy (TEM) and EET results for powders heated at 950°C showed an average particle size of about 37nm [Li90].

Wakui and Werning did a study on single phase gels derived from an aluminum nitrate nitroxydian TEOS molecular sol [$Hu90$ and $Hu93$]. Two types of gel were produced: fresh gel and aged gel. The fresh gel was prepared by rapid droplet drying of the molecular sol in a heater heated to 100°C. The aged gel was prepared from the fresh gel by exposing it to a humid environment at 40°C.

Differential thermal analysis of the fresh gel showed an endothermic peak at 950°C [Hu93]. X-ray diffraction analysis for samples heated just above 900°C

showed nearly complete crystallization to the monoclinic *iso*-isomorph-mullite($2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$). Analysis using TEM showed the presence of a glass-rich amorphous phase enveloped by isomorph-mullite.

Differential thermal analysis of the aged gel showed a prominent exothermic peak at 950°C . In addition, a broad weak peak was observed at 447°C . X-ray diffraction analysis of samples heated just below and just above 447°C showed that the DTA peak at that temperature corresponded to crystallization of *iso* with orthorhombic mullite ($2\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$). It was observed that by increasing the heating rate at which the DTA was performed, the 447°C peak shifted to lower temperatures. Further, while the intensity of the 447°C peak increased with higher heating rates, the intensity of the 950°C peak decreased.

Single phase gels were also prepared by Schmidt and co-workers [14b]. Aluminum isoplate (71 wt%) was mixed with TEOS (38 wt%) in the presence of isopropanol as a solvent. Water was added dropwise to the mixture, and a white gel was produced. Differential thermal analysis showed a sharp exotherm of high intensity at 940°C , in addition to a weak exotherm at 1230°C . X-ray diffraction analysis for samples heated at 1200°C showed the presence of γ - Al_2O_3 mullite, and small amounts of cristobalite. Mullite was the only phase observed for samples subsequently heated to 1400°C and 1600°C .

The use of chelating agents in the processing of single phase mullite gels was studied by Henschel and co-workers [14c]. Their system consisted of aluminum-*iso*-borylate, *p*-diketone, triethylcarbonate, isopropanol and hydrochloric acid.

Acetylacetone (AcAc), methylalumoxane (MAO), and ethylalumoxane (EAo) were used as the β -diketonates. The molar ratio, R, of β -diketonate to aluminum-oxo-isopropylate was varied from 0.5 to 2.0. A solution of β -diketonate and isopropanol was added dropwise to the aluminum-oxo-isopropylate solution. A solution of TEOS and isopropanol was added thereafter. Hydrolysis was carried out by adding an aqueous HCl solution.

It was shown that particle size was a function of the amount of β -diketonate used. The particle radius measured was a function of the number of condensation sites per aluminum atom which were blocked by β -diketonates after hydrolysis. The more condensation sites blocked the smaller the particles.

The gelation time was found to be dependent on the amount and type of chelating agent. The gelation time increased as the amount of β -diketonate increased and the larger the molecular size of the chelating agent. Nuclear magnetic resonance (NMR) results showed the presence of Al-O-Si bonds during all stages of gelation. The MAS-NMR spectra showed that it was possible to obtain homogeneous gels on a molecular scale using chelated aluminum chloride.

Continuous Membrane Fibers Using Sol-Gel Processing

The main problem associated with sol-gel processing is the difficulty in producing large shapes because of the cracking introduced by drying stresses associated with capillary forces, and shrinkage stresses during drying [LaChen]. These effects are minimized with fibers because the diffusion distances are small and

stress can be relieved by local bending of the fiber. These factors are effective after forming the fibers from the sol, however, formation of fibers from the gel is a difficult task. Production of good quality continuous textile fibers requires achieving certain rheological conditions that are essential for continuous spinning.

Prior to the use of sol-gel processing, ceramic fibers were produced from molten oxides [Kowalski]. The liquid phase required specific rheological properties to enable spinning of fibers, as a result, compositions were limited to certain grades or mixtures of oxides. Consequently, high percentages of SiO_2 were often needed in the fibers, and this limited their use at high temperatures.

Sol-gel processing can be used to produce fibers in the sol stage. This expands the range of compositions of ceramic fibers to include a variety of compositions that were not possible using the melt method. As a result, fibers that possess good creep resistance, chemical durability, and high tensile strength can be produced. Another advantage of sol-gel processing of fibers over spinning of molten oxides is the lower processing temperatures. Fiber spinning using the sol-gel method is usually carried out at room temperatures which is more economical and technically more controllable than high temperature spinning.

Hosfield and co-workers investigated the processing of continuous textile fibers from polymeric sols [Hosfield]. The first step in the process was the production of polyethoxysilanes. The polyethoxysilanes was prepared by partially hydrolyzing and polymerizing an aluminum alkoxide. Triethylaluminum was polymerized in ether with an equimolar amount of water which was added dropwise at 20-40°C. The

polymerization process was monitored by measuring the amount of C_2H_4 produced. The degree of polymerization was controlled by changing the amount of water added. A polymeric silica sol was then mixed with the polysiloxane to form a silica sol.

The amount of silicon-containing compound to be mixed with the solution of the polysiloxane was found to affect the spinning of the sol. When a silicon-containing compound with no spinability was added in large amounts to the polysiloxane, the spinability of the resulting solution was poor.

The silica sol was spun through 70-100 micron holes. The atmosphere in which the spinning was carried out was controlled. Solvents contained in the fiber were removed during or after the spinning step. The spun fibers were hydrolyzed by moisture contained in the air, and then were fired for the purpose of maturation and sintering. Fibers produced at temperatures below 1250°C had good strength. On the other hand, fibers fired in the 1250°C-1500°C range were brittle and had low strength due to an exaggerated growth of silica grains. As a result, the use of these fibers at high temperatures was limited.

Kern and Seeman investigated the processing of continuous silica fibers from diphenyl gels [Ref. 7]. The silica sol was prepared by adding aluminum isopropylate to a mixture of formic acid and deionized water. Aluminum formate was added to the mixture with subsequent heating to 60°C until the solution was clear. Following this, aqueous colloidal alumina, aqueous colloidal silica, and latex paint were added to the mixture. The resulting sol was then concentrated under a vacuum. The sol was extruded through a spinneret after the

spinning manually was relieved. The stretched fibers were drawn vertically downward through the center of a dipper stick in a countercurrent stream of dry air introduced near the bottom end of the stick. The fibers were then fired at 550°C to remove physical water and other volatiles. Following initial firing, the fibers were heated to 850°C to remove residual volatiles and induce crystallization. After heating to 850°C, a solution of 0.5 wt% hexamine-cooperate Mott copolymer rubber and 2.5 wt% mineral oil was applied to the fibers before winding them on a drum.

Samples fired to 1500°C had a tensile strength of about 8-9 GPa. X-ray diffraction analysis showed that fibers fired at 1500°C for less than 10 sec, showed a maltese phase with traces of alumina. After periods of time longer than 15 sec at 1500°C, maltese was the only phase detected.

Processing of random maltese fibers was also investigated by Tucker and co-workers [Tuc78]. The silica sol was prepared by hydrolyzing TEOS. The hydrolysis step was carried out in the presence of distilled water, hydrochloric acid, and isopropyl alcohol. The mixture was allowed to react at 40°C for 90 min. Hydrolysis of the aluminum mixture followed. The aluminum precursor was aluminum diisopropoxide acetoacetic ester-chelate (ADC). The chelate provides a greater possibility for the formation of the linear polymer necessary for production of a spinnable fiber, as it allows two reaction sites for the ADC. The aluminum sol components, ADC, hydrochloric acid, water, and isopropyl alcohol, were mixed slowly to form a homogeneous solution. The aluminum and silica sols were then mixed at

40°C in a nitrogen atmosphere. Sponable gels were extracted from the gel at time periods ranging from 4 hours to 5 days.

In the spinning process, the fibers, after being extruded, were passed through an air gap in a bath containing deionized water and polystyrene oxide. The pH of the bath was adjusted by adding sodium hydroxide. The bath was used to collapse the fibers and to improve the structural integrity. Fibers with a large diameter, 110 microns, were spun. After firing at 1200°C, pure sponable fibers were obtained. However, the fibers exhibited porosity and microcracks, and were very brittle, as a result.

The use of sponable gels to produce smaller fibers was studied using two methods by Venkatasubramanian et al. [Ven98]. The two methods differed in the choice of precursor materials used as the source of alumina and silica. Aluminum hydroxychloride hydrate and LUDOX-40 colloidal silica were the starting materials for method I. Aluminum formate hydrate and LUDOX-C1 colloidal silica were the starting materials for method II. Another processing difference was that in method I fibers were drawn by hand, while in method II, fibers were prepared by centrifugal spinning.

Gas adsorption measurements indicated that the average pore size for method I fibers fired at 1000°C was about 4 nm. An average pore size of 3.3 nm was observed for method II fibers fired at 900°C. The finer pore structure of method II resulted in a more rapid desiccation. It was believed that desiccation of fibers occurred by a viscous flow mechanism in both methods.

X-ray diffraction analysis showed that molten multicomponents occurred above 1100°C for both methods. Fibers from both methods fired at 1500°C showed grain sizes below 1 μm . Examination of grain boundaries of method I fibers via TEM did not show the presence of a glass phase, as similar analysis was done on method II fibers. However, another method could be used to produce solutions with the necessary properties for continuous fiber spinning.

Kishinev and co-workers investigated the effect of additives on microstructure and crystallization of molten $\text{BaO} \cdot \text{P}_2\text{O}_5$. The chemical sol was made by dissolving aluminum powder in a mixture of orthophosphoric acids. A stoichiometric amount of $\text{H}_2\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ was added to the chemical sol. The additives investigated were B_2O_3 , P_2O_5 , and Cr_2O_3 . They were added as boric acid, phosphoric acid, and chromium anhydride, respectively. Lactic acid was added to adjust gelation.

The sol was concentrated to a viscosity of 100 to 150 dS/cm^2 , and then pressure extruded through a spinner. The fibers were drawn after extrusion through a drying chamber to form continuous filaments. Differential thermal analysis was used to determine transformation temperature. For the unmodified molten fibers, an endothermic reaction with a peak at 810°C was confirmed by XRD to correspond to the formation of a crystal phase. A second endotherm observed at 1280°C was confirmed to correspond to molten formation.

Addition of low-temperature glass formers such as B_2O_3 and P_2O_5 produced sharper endotherms and raised the crystal formation temperature to 917°C and 984°C, respectively. On the other hand, the addition of B_2O_3 and P_2O_5 lowered the molten

formation temperature to 1225°C and 1251°C, respectively. Addition of Cr_2O_3 did not appear to have an effect on spinel and malin formation temperatures.

Transmission electron microscopy micrographs of the unmodified malin fibers heated to 1200°C and held for 1 hr showed grain size of 4000 Å, intergranular pore size of 250 Å, and intragranular pore size of 100 Å. Fibers that contained B_2O_3 had the smallest grains and the most uniform grain size distribution. Grain sizes of 400–1000 Å and pore size of 200 Å were observed for fibers containing B_2O_3 . In addition, B_2O_3 fibers were denser than those of any other composition studied. On the other hand, addition of Cr_2O_3 or $(\text{B}_2\text{O}_3 + \text{Cr}_2\text{O}_3)$ resulted in grain size larger than that of the unmodified malin fibers.

Room and *ex-situ* studied formation of malin fibers from polymeric sols [Katz]¹² The starting sol was prepared by reacting aluminum sec-butoxide with isopropanol, and acetylacetone. The mixture was then hydrolyzed and polymerized by adding water and hydrochloric acid. The silica sol was prepared by adding TEOS, isopropanol, water, and hydrochloric acid. After mixing the two sols, a crosslinking step was carried out inside an 80°C oven for 56 hr. The crosslinking time was reduced to 24 hr by using a rotary vacuum evaporator and a vacuum drying oven. Extrusion of fibers was accomplished by drawing fibers through a 300–600 μm hole spinneret.

Viscosity measurements of the malin sol revealed that for the acetylacetone to aluminum-sec-butoxide molar ratio (R_1) of 1.5, the viscosity increased dramatically after 56 hr. Gradual increases in the viscosity were observed for R_1 values of 1.5 and

6.1. The rheological behavior of the oil is a function of time and deformation. Shear thickening behavior was observed after 40 hr, shear-thinning behavior after 50 hr, and a pseudoplastic or shear-thinning flow behavior after 60 hr.

Differential thermal analysis results indicated that molten boronates occurred at 1600°C. X-ray diffraction analysis for samples heated to 1300°C showed the presence of a molten phase. Micrographs taken by SEM showed that the fibers had a needle-like microstructure.

Commercially Available Molten Fibers

Model 440 and 440 are among the commercially available molten fibers. Model 440 fibers contain 70% Al_2O_3 + 20% B_2O_3 + 20% SiO_2 (flowed). They have a tensile strength of 1.72 GPa and modulus of elasticity of 207-241 GPa. Fibers heat treated at temperatures up to 1600°C retained their strength. Fibers heat treated beyond 1600°C showed a significant degradation of properties. Model 440 fibers contain very small crystallites in the range of 20 to 40 nm in size.

Model 440 fibers have a 3 to 2 aspect ratio of diameter to radius [Johari]. The average grain size was shown to be 150 nm. The fibers retained about 75% of their strength through a heat treatment temperature of 1000°C, and 40% strength remained after 1400°C (these fibers were tested at room temperature). High temperature strength measurements showed that the strength remained almost constant up to about 600°C then fell to about 40% of its initial level at 1300°C. The fiber strength at 1250°C was about 1.3 GPa. The measurement of the elastic

modulus at high temperatures showed a significant drop above 800°C. At 1100°C, the modulus was approximately 10% of its initial value. These fibers show a distinct amorphous glass phase.

Five alumina-silica fibers were developed by Solvaco chemists. The composition of the fibers is 85 with alumina and 15 with silica [Lentz]. The microstructure consists of very small $\gamma\text{-Al}_2\text{O}_3$ crystallites homogeneously mixed with an amorphous silica phase. The fibers were processed by polymerization of metal alkoxides. The fibers were heated to 700°C to remove organics. The final step was heating the fibers to 910°C to complete the formation of $\gamma\text{-Al}_2\text{O}_3$.

High temperature strength and elastic modulus measurements showed a drop in the strength and the modulus above 800°C. The elastic modulus at 1100°C was about 40% of its original value. Measurements of the creep rate indicated that the fiber crept at temperatures above 600°C, and that the creep rate increased rapidly with temperature. The degradation in the mechanical properties was attributed to the softening of the amorphous silica matrix in which the alumina crystallites were embedded. Transformation to mullite was noticed for fibers heated above 1120°C.

CHAPTER 3 SOL-GEL PROCESSING

Introduction

The term *sol-gel* is used to describe a variety of chemical systems of inorganic materials. The process owes its name to the rapid viscosity increase that occurs after sol fabrication or during aging [Bald]. The sol is a system in which separate chemical species (solids and solvent) are sustainable. If the solution or suspension conditions are changed slightly, demulsification can occur [Jordil]. The demulsification of the sol can result in precipitation of the sol species as aggregated or aggregated particles or the formation of a homogeneous gel.

The gel consists of a continuous solid network enclosing a continuous liquid phase [Bald]. The gel has an elastic character which is introduced by the continuous solid network. The sol-gel technique involves physical and chemical processes associated with hydrolysis, polycondensation, drying, delatation, and densification. The advantages associated with sol-gel processing are [Bald]

- very high purity,
- better homogeneity compared to powder mixing technology,
- low processing temperatures compared to traditional ceramic processing techniques,
- uniform phase distribution in multicomponent systems,
- easy preparation of coatings and thin films,

- better size control in powder synthesis, and
- the ability to produce new crystalline and non-crystalline solids

Although sol-gel processing has many advantages, it also has some disadvantages, such as [Burdick]

- the high cost of raw materials,
- large shrinkage during processing,
- residual porosity,
- residual hydroxyl groups and carbon,
- health hazards associated with the organic solvents, and
- long processing times.

Sols can be divided into two major categories, colloidal (particulate) sols and macromolecular (polymeric) sols. A colloidal sol is a solution that contains dense oxide particles [Daulton and Brink]. A macromolecular sol is a solution of macromolecules that are obtained by the hydrolysis and polycondensation of metal alkoxides.

Colloids are solid particles with diameter of 1 nm to 100 nm [Wicks]. A colloidal system is a dispersed or heterogeneous system consisting of at least two phases, one of which is a dispersed phase and is uniformly distributed within a continuous phase (the dispersant medium) [Wicks].

A polymer, or a macromolecule, is a large molecule formed from monomers that are capable of forming at least two bonds [Burdick]. Metal alkoxides $M(OR)_3$ are derivatives of alcohols (ROH)-in which the hydrogen of the hydroxyl group has been

replaced by a metal $(\text{OH})^-$. Metal silicates can also be considered as derivatives of metal hydroxides, $\text{M}(\text{OH})_n$ [Dau79]. Colloid stability is an important aspect in the processing of colloidal sols. An understanding of the different forces acting on the colloids is essential when studying the stability of colloidal sols.

Stability of Colloidal Sols

The stability of colloidal sols is a function of a combination of factors. These factors are presented in the following sections.

Surface Energy

From the first and the second law of thermodynamics, for systems with a phase interface separating the bulk phases [Dell94]:

$$d(E - TS - P'V + \gamma A) = \sum_i \mu_i dn_i + \sum_j \mu_j dN_j \quad (2.1)$$

where

E = internal energy,

T = temperature, S = entropy,

P = pressure, V = volume,

γ = surface tension, A = surface area,

μ_i = chemical potential of element i ,

and n_i = number of moles of element i .

Introducing the Gibbs free energy G , where G is

$$G = U + P^*V - TS \quad (2)$$

The decrease of the Gibbs free energy, dG , can be calculated as

$$dG = -SdT + PdV + \sum_i \mu_i dn_i + \sigma dA \quad (3)$$

The surface tension of a solid can be defined by the reversible work done in creating a new surface or by adding or removing atoms to or from the surface [Kau]. The surface tension relative to the free energy and the internal energy can be defined as

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{T, P, n_i} = \left(\frac{\partial U}{\partial A} \right)_{T, P, n_i} \quad (4)$$

Where ∂ represents the partial-derivative, and the subscript refers to the independent variables which have to remain constant during the increase in surface area by a unit amount.

The source of the surface free energy arises from the broken or distorted bonds of surface atoms. These atoms are only partially surrounded by neighboring unit atoms. These broken or distorted bonds result in an increase in surface energy [Kau].

From the above discussion it can be seen that the higher the surface area, the higher the energy state of the surface particles. Since systems tend to maintain a low energy state, there is a tendency to lower the surface area.

As mentioned earlier, colloids are very small solid particles with diameters, of 1 - 100 nm. Assuming that the colloids are spherical, the surface area to mass ratio is

$$\frac{SA}{M} = \left(\frac{3}{\rho r} \right) \quad (2.2)$$

Where SA is the surface area, M is the mass, ρ is the density, and r is the radius. This means that for the same mass, the surface area of two spheres is larger than the surface area of one sphere. Therefore, there is a tendency for the colloids in the solution to collapse, or to come to one another and coalesce to reduce surface area, and as a result, reduce the surface energy [Joshi].

The process of coalescence is driven by the difference in the solubility between surfaces of different curvatures. Particle surfaces have positive radii of curvature, while neck regions (formed during coalescence) have negative radii of curvature. The solubility is related to the radius of curvature by [Hirth]

$$S = S_0 \exp \left(\frac{\gamma_{SL} V_m}{RT} \right) \quad (2.3)$$

where

- S_0 = solubility of a flat surface of the solid phase
- γ_{SL} = solid-liquid interfacial energy
- V_m = molar volume of the solid
- R = gas constant

T = temperature

r = particle radius

The equation shows that positive nuclei have high wettability while negative nuclei have low wettability. As a result, the material dissolves from the particle surface and re-precipitates in the bulk region. This process is similar to the evaporation-condensation process which will be discussed later in this study.

Colloids or suspensions exhibit Brownian motion. Brownian motion is introduced by the constant collision of liquid molecules with colloids [36]. The effect of these collisions on the movement of the colloids is inversely proportional to the size of the colloid. These moving colloids collide with each other and they may stick to each other due to the strong Van der Waals attractive forces.

Van der Waals Forces

"Van der Waals forces are short range secondary attraction forces which originate through electrical dipoles inside or on the surface of a material." [36]. If an electrical dipole, the centers of negative and positive charges are displaced with respect to each other. The presence of displaced center of charges allow the molecules forces to become functional. Electrical dipoles are either inherent or induced. Electrical dipoles are inherent in asymmetrical molecules. Dipoles can be induced by an electric field that is either applied externally or applied by a neighboring ion, molecule or atom. This means that even symmetrical structures

develop Van der Waals interactions. Van der Waals interaction forces are relatively weak for induced dipoles. Another type of dipole is the transient dipole.

The Van der Waals forces arise from three types of interactions [DeHo and Hillel]:

- = permanent dipole with permanent dipole (Keesom forces),
- = permanent dipole with induced dipole (Debye forces), and
- = induced dipole with induced dipole (London forces).

The third interaction occurs only when two atoms are in close proximity. The electrons of the two atoms will redistribute so as to maximize the energy of the system, producing two dipoles and resulting in a net attraction force. The total interaction force between molecules is the sum of all three mechanisms. The potential energy of attraction two spheres, U_A , is [Ree73]

$$U_A = -\frac{A}{16\pi} \quad (3)$$

where:

- A = Hamaker constant
- a = particle diameter
- h = separation distance

The Van der Waals attraction forces can result in aggregation upon particle contact. Repulsion forces have to be induced to prevent aggregation of collicids.

Electrostatic Repulsion

One method used to prevent or reduce aggregation is the development of electrostatic repulsion. The net force between particles in suspension is assumed to be the sum of the attractive Van der Waals forces and the electrostatic repulsion created by the induced surface charges. The repulsive barrier depends on the type of ions in the electric double layer. The electric double layer is the region adjacent to the surface of the colloid which contains the charge-determining ions (those positioned on the colloid surface) and the counterions (those positioned on the adjacent surface). The counterions act to neutralize the surface charges.

Surface charge can be achieved by the following techniques [Rao84]

1-Chemical reaction with an aqueous medium. In this process the sign of the surface charge is determined by the pH of the solution [Kro86]. For hydroxyl moieties, the charge-determining ions are H^+ and OH^- . The charge is created by protonating or deprotonating the MOH (metal hydroxide) bonds on the surface of the particle. The pH at which the particle is neutrally charged is called point of zero charge (PZC). In the case of pH less than PZC, i.e. acidic conditions, the MOH group is protonated and a positive charge is acquired [Bis86]



When the pH is greater than the PZC (basic conditions), the MOH group is deprotonated and a negative charge is acquired



The magnitude of the surface potential, ψ_0 , depends on the value of pH relative to PZC.

3- Adsorption of specific ions: In this process, the surface develops a charge due to the preferential adsorption of particular ions from the solution [Pearce]. Ions are adsorbed on oppositely charged surfaces [Pearce]. In some cases, complete adsorption of ions can lead to neutralization of the surface charge, as shown in this reaction:



The adsorption of multivalent ions may lead to surface charge reversal:



Where $a > 1$.

3- Desorption and dissolving: This process depends on the difference in the dissolution rate of the different ions in colloid particles [Pearce]. If the colloid is composed of two ions species then it is likely that the anions and cations will dissolve at different rates [Pearce]. The surface will have a high concentration of the ions with the lower dissolution rate, and a low concentration of the ions with the higher dissolution rate. As a result, the charge of the lower dissolution rate ions will dominate the surface charge.

The Structure of The Electric Double Layer

The distribution of ions and polar liquid molecules is influenced by the surface charge of the colloid in solution. Coulomb forces repel like-charges and attract polar liquid molecules and oppositely charged ions into a region near the surface increasing their concentration relative to the average in solution (Fowell). The potential gradient in the double layer is not sharp, because thermal vibrations of molecules in the liquid cause the diffusion of counterions. The diffusion of counterions due to molecule thermal vibrations is more significant at high temperatures. The double layer can be divided into two regions, the Stern layer and the Gouy or diffuse double layer (Brink). The Stern layer is the region adjacent to the charged surface that contains a tightly bound layer of counterions. The diffuse layer is the region beyond the Stern layer in which the counterions and polar liquid molecules diffuse freely. The plane separating the Stern and the Gouy layer is called the Helmholtz plane.

Charged colloids move when an electric field is applied (Brink). As they move, they carry along the attached layer and part of the counterions close. The rest of the counterions (the more distant portion of the double layer) move in the opposite direction. The plane that separates the fluid that moves with the particle from the region that flows freely is called the slip plane or plane of shear. The potential at the shear plane is referred to as the zeta potential. The point at which the pH is equal to zero is referred to as the isoelectric point (IEP) (Brink).

The potential drops linearly through the Stern layer. A model for the potential gradient in the diffuse double layer was developed by Gouy and Chapman (Rush¹). This model is based on a uniformly charged surface, a solution with uniform dielectric constant, and point charges. Assuming that the distribution of charges in the diffuse layer follows Boltzmann's equation, the concentration of counterions in the diffuse layer, N_d , relative to the concentration of counterions adsorbed on the surface, N_{ad} , is given by the following ratio:

$$\frac{N_d}{N_{ad}} = \exp\left(-\frac{qU_p}{k_B T}\right) \quad (1.12)$$

where U_p is the potential energy of the ion, k_B is Boltzmann constant, and T is the temperature.

The potential in the diffuse layer ψ , where the surface potential $\psi_s \leq 100$ mV, can be defined with respect to the surface potential as (Rush¹)

$$\psi = \psi_s \exp\left(-\frac{x}{\lambda_D}\right) \quad (1.13)$$

where x is the distance from the charged surface, and λ_D^{-1} is the Debye-Hückel screening length (Rush¹). The thickness of the double layer is the distance from the charged surface to the plane where $\psi = \psi_s / 1.716$. The thickness of the double layer is calculated from the equation (Rush¹)

$$\lambda_D^{-1} = \left(\frac{4\pi e^2 \sum_i N_i z_i^2}{\epsilon^0 \epsilon} \right)^{1/2} \quad (1.14)$$

Where ϵ is the solvent dielectric constant, ϵ_0 is the vacuum permittivity, F is Faraday's constant, N_1 is the concentration of ions of type 1, and V_1 is the volume of counterions of type 1. Equation 3.14 shows that increasing the volume or the concentration of the counterions leads to compression of the double layer. On the other hand, increasing the temperature or the solvent dielectric constant leads to an expansion of the double layer.

The interaction of two particles with identically charged double layers is described by the DLVO theory [H-90]. The theory assumes that the net force between particles is the sum of Van der Waals attraction forces and the electrostatic repulsion forces created by the interaction of the double layers. The form of the repulsion depends on the size and shape of the particle, the distance (R) between their surfaces, the double layer thickness, and the dielectric constant of the solvent. For two spherical particles of diameter a , and for $ka \ll 1$, the potential energy of repulsion is [H-90]

$$U_R = \frac{4\pi\epsilon_0\epsilon a^2}{3\phi(1+\phi)} \exp\left(-\frac{R}{\lambda_D}\right) \quad 3.15$$

The repulsion energy increases with increasing surface potential, solvent dielectric constant, and double layer thickness.

The total potential energy, U_D , is the sum of the attractive potential energy (from Van der Waals forces) and the repulsive potential energy:

$$U_D = U_A + U_R \quad 3.16$$

Therefore, from equations 3.7 and 3.13, the total potential energy is

$$U_{\text{tot}} = -\frac{da}{2ab} + \frac{na^2V_c^2}{a^2(b+1)} \exp\left(-\frac{h}{b+1}\right) \quad (3.17)$$

For the case of $h \gg 1$, the potential energy of repulsion becomes

$$U_{\text{rep}} = \frac{na^2V_c^2}{b} \ln(1) + \exp\left(-\frac{h}{b+1}\right) \quad (3.18)$$

Colloidal Stabilization

Coagulation can be prevented by using polymers. The spatial extension of high molecular weight polymer molecules is usually comparable to or greater than the range of the Van der Waals interaction between colloids [Nap03]. Therefore, polymer molecules have the correct dimension to impart colloidal stability. There are two types of polymer stabilization, depletion stabilization and steric stabilization.

In depletion stabilization, colloidal particles are separated by free polymer chains (i.e., the polymer chains are not adsorbed on the colloidal surface) [Nap03]. Depletion stabilization requires a high concentration of free polymer in the liquid. Low free polymer concentration may result in flocculation.

In steric stabilization, the macromolecules are adsorbed on the surface of the colloid. The adsorbed layer of macromolecules retards close approach of the particles in two ways, osmotically and enthalpically [Brink]. When colloids approach each other, the entropy drops as a consequence of the overlapping of chains from

different solvents. This reduced entropy results in a restriction of freedom of motion of the chains. In addition, when the polymer chains overlap, the solvent around the chains is compressed, expending energy. As a result, a pressure difference is created that pulls the solvent back into the space between the particles causing the particles to be pushed apart.

In order to have an effective steric barrier, certain requirements must be met [1819]. First, the polymer chains should be strongly attached to the surface, and second, the surface of the particle should be completely covered with the polymer. In addition, the polymer chains must be long enough to keep the point of chain approach outside of the range of the attractive Van der Waals forces.

Sol-Gel Processing Steps

Sol gel processing of materials requires following certain steps. Each step can have a significant effect on the properties of the final product. These steps are hydrolysis and polycondensation, gelation, aging, drying, deliquescent, and sintering.

Hydrolysis and Polycondensation

Hydrolysis and polycondensation are the reactions responsible for structure evolution in sol-gel processing. Hydrolysis and polycondensation can be used for processing of both, colloidal and polymeric sols. In order for polycondensation to occur, hydrolysis must first take place. Hydrolysis and polycondensation can occur to both inorganic precursors and metal-alkoxides.

Hydrolysis and Coordination of Inorganic Precursors

Hydrolysis of inorganic precursors is carried out by the dissolution of salts in water. The dissolution of salts yields cations and anions. The metal cations, interact with the water by the following reaction [R790]



Depending on the water acidity, coordination number, solubility, electropositivity of the metal and pH of the solution, the following hydrolysis reaction takes place [R790]

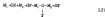


where $M(OH)_x$, $M-OH$, and $M=O$, are aquo, hydroxo, and oxo complexes respectively. The electropositivity is a measure of the atom's ability to attract electrons and it is proportional to the sum of the energy to add an electron and the energy to remove an electron from the neutral atom [R790]

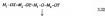
At the same pH, different complexes can result depending on the metal cation [R790]. For a pH of 7, hydrolysis yields aquo complexes for a metal valence above +6 and aquo-hydroxo for a metal valence below +3. Also, at the same valence, changing the pH results in different hydrolysis products. For example, hydrolysis of cations with $x = +6$ yields hydroxo, complexes at low pH values (below 1.5), and oxo complexes at high pH values.

Coordination can occur by either nucleophilic substitution or nucleophilic addition in the processing of inorganic salts. Nucleophilic substitution takes place

when the preferred coordination is satisfied [B-20]:



Nucleophilic addition takes place when the preferred coordination is not satisfied [B-20]:



Condensation by nucleophilic addition occurs when one of the reactants has a maximum coordination number (N) lower than the available sites (n) (i.e., one of the reactants is coordinatively unsaturated). Except in the case of coordinatively unsaturated precursors, it is necessary to have hydroxyl complexes to generate condensed species. This can be accomplished by adding a base to aqua-complexes or by adding an acid to aqua-complexes.

Condensation can take place through other reactions. Coordinatively saturated hydroxyl-aqua precursors undergo a nucleophilic substitution reaction to yield a hydroxy bridge between two metal ions. This condensation reaction is called *linkage* [B-19]. Coordinatively saturated metals can also undergo a nucleophilic reaction followed by water elimination to yield an-oxo bridge between the metal ions. This condensation reaction is called *oxidative* [B-19]. For coordinatively unsaturated metals, oxidation takes place by nucleophilic substitution,

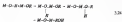
Hydrolysis and Polycondensation of Metal Alkoxides

Metal alkoxides in general, and transition metal alkoxides in specific, are very reactive species. The high reactivity is due to the presence of highly electronegative alkoxy groups making the metal atoms vulnerable to nucleophilic attack [Ercik and Sathya]. The hydrolysis of metal alkoxides results in the formation of hydrides or hydrated oxides [Ercik]. When limited amounts of water are added, these metal alkoxides undergo partial hydrolytic reaction producing as some cases products of certain composition or oxide alkoxides.

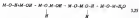
Silicon alkoxides are considered far less reactive than transition metal alkoxides for the following reasons [Ercik]:

- Transition metals are more electrophilic due to their low electronegativity. This results in the transition metals being less easily started nucleophilic reactions such as hydrolysis and polycondensation.
- Transition metals often possess several stable coordination, and if coordinately unsaturated, they are able to increase their coordination by condensation reactions.

The high reactivity of most metal alkoxides requires that they would be processed with strict control of moisture and other conditions of hydrolysis in order to prepare homogeneous gels. A comparison between silicon alkoxide and aluminum alkoxide is a good example of the effect of the electronegativity value. Silicon has an electronegativity value higher than that of aluminum [Ercik]. As a result, aluminum alkoxides have higher hydrolysis and condensation rates than silicon



If the condensation reaction by-product is water, then the reaction is called **oxidative** [10/10]



For coordinatively unsaturated metals, coordination occurs by means 18-20



The kinetics of cleavage are faster than kinetics of alcoholysis and methanolysis, since no proton transfer occurs in the transition state of cleavage. In addition, cleavage has lower enthalpy because $\Delta H^\ddagger = 2.3$ kcal/mol.

The reaction of metal alkoxides, before or during hydrolysis and polycondensation, with alcohols, β -ketoesters, alkenesulfonates, and acid or base catalysts is of significant importance. Studying the reaction of these diamazoles with metal alkoxides is important to understand growth and structure evolution in the sol-gel processes.

Metal Alkoxide Reaction with Alcohols

The type of solvent used in the sol-gel process has an important effect on reaction kinetics. Alkoxide reactivity can be modified by changing the solvent [Rus83]. The reaction of alkoxides with alcohols is called alcohol interchange reactions or alcoholysis which can be represented by the following equation [Rus78]:



The rate with which the alkyl group is interchanged is a function of the size of the alkyl group. The rate of interchange decreases from primary to secondary to tertiary groups [Rus78]. The methyl group has a higher interchangeability than the ethyl group, which in turn has a higher interchangeability than the *iso*-butyl group. Alcoholysis is also susceptible to steric factors. Bradley showed that the rate of exchange is slow in a mixture of titanium *tert*-butoxide and *tert*-butanol [Bra76]. On the other hand, the rate of exchange is fast in a mixture of titanium *tert*-butoxide and *tert*-butanol. The difference in the exchange rate was attributed to steric effects.

Reaction of Metal Alkoxides with *p*-Siloxanes

p-siloxanes are chemically with molecules that have a reactive hydroxyl group. These molecules react readily with metal alkoxides through one of the following reactions [Rus78]:





p-Dicarboxylic acids (ADA), isophthalic acids, and ethyl acetoacetic are examples of *p*-dicarboxylic acids.

p-Dicarboxylic ligands are more resistant to hydrolysis and polycondensation than chloride groups. They are used to block hydrolysis sites, accordingly, they are called chelating agents. Chelating agents are used to prevent precipitation of rapidly reacting chlorides. They are also be used to specify certain functionality for the metal ions, i.e. allow coordination to occur on certain sites in order to achieve a certain structure, like the growth of one-dimensional polymers which are suitable for fiber drawing.

The addition of chelating agent has an effect on gelation time [He04]. The gelation time increases with the increase of the amount of the chelating agent. Also, the gelation time increases with the increase of the molecular size of the chelating agent. The amount of chelating agent has an effect on particle size. Larger amounts of chelating agents result in smaller particle size due to the large number of blocked coordination sites.

Reaction of Metal Alkoxides with Alkoxycarbonyls

"Alkoxycarbonyls are derivatives of alcohols from which the hydrogen atoms of alkyl or aliphatic groups have been replaced by two atoms or halogen substituted amino groups" [He04]. Examples of alkoxycarbonyls are ethoxycarbonyl, dioxanocarbonyl, and triethoxycarbonyl (TEA). Like *p*-dicarboxylic acids, alkoxycarbonyls are

be used as chelating agent to control the degree of hydrolysis and polycondensation [Ref1] and [Ref2].

Two types of results can be produced when siloxanes react with metal alkoxides. Some metal alkoxides show reactivity with only the hydroxyl groups of the siloxanes and simple derivatives are obtained [Ref3]:



In other metal alkoxides, both the hydroxyls as well as the silicon groups of the siloxanes undergo replacement reactions with metal alkoxides to form cyclic structures [Ref4]:



Role of Acid and Base Catalysts

Acid and base catalyst have an important role in sol-gel processing. Acid catalysts are used to enhance the process kinetics. The acid role is to protonate negatively charged siloxide groups, eliminating the requirement for proton transfer within the reaction zone [Ref5].



The rate of protonation varies for different alkoxide ligands. The inclination of protonation decreases as the electron providing power of the ligand decreases in the order, alkoxy, hydroxy, oxo [Ref6]. As a result, auto-catalyzed condensation is

directed toward the ends of the chain. This means that acid catalysis results in long polymer chains with little branching.

The rate of base catalysis is to deprotonate the hydroxyl ligands [Ref.9].



Generally, base catalysis enhances condensation kinetics. The reactivity toward nucleophilic attack is higher in the middle of the chain than at the ends. This means that condensation is directed toward the middle rather than the ends of the chain. Consequently, more compact and highly branched species are produced.

Definition

As time proceeds after hydrolysis and polycondensation, clusters start growing either by aggregation of soloids (i.e., colloidal sols) or by linking polymer chains by esterification reactions (i.e., polymeric sols) [Ref.10]. The clusters continue to grow until they collide and link together to form a single cluster. This single cluster is referred to as the gel. The gel can support stresses elastically, i.e., with no irreversible deformations [Ref.10]. The time required to reach gelation point is called gelation time.

The rheological conditions of a gel include Newtonian behavior ($\dot{\gamma} = \eta \dot{\gamma}'$), shear thinning behavior ($\dot{\gamma} = \eta \dot{\gamma}'^n$), and shearthick behavior ($\dot{\gamma} = \eta \dot{\gamma}'^n$), where $\dot{\gamma}$ = shear stress, η = viscosity, $\dot{\gamma}'$ = shear rate, and n = power term [Ref.11]. Sachs and Allen investigated the changes in viscosity as a result of structural changes during

aging of silver gel [SachT]. It was shown, that initially, the gel exhibited Newtonian behavior (the viscosity is independent of shear rate). The gel behaved this way because there was no significant particle-particle interaction due to low particle concentration.

The Newtonian behavior was followed by shear thinning behavior (the viscosity decreases with the increase of the shear rate) for gels aged for a longer period of time. This behavior is due to the presence of large agglomerates that immobilize liquid resulting in high viscosity at low shear rates. At high shear rates, the agglomerates break releasing the entrapped liquid, and resulting in a decrease in the viscosity.

Further aging resulted in thixotropic behavior (yield behavior with hysteresis). The long aging time results in the formation of a three-dimensional network through condensation growth and agglomeration. A yield stress in the shear rate versus shear stress relation was observed due to the elastic character of the network. After the yield stress is exceeded, shear thinning behavior accompanied by hysteresis was observed. This behavior indicates that the network structure is broken down as the shear rate is increased, but full recovery does not occur when the shear rate is decreased.

Aging

The consumption of chemical reaction after gelation is referred to as aging [Hess90, Br90]. Aging is carried out at room temperature or under hydrothermal

continues by increasing the gel to post liquid. Aging results in crosslinking, swelling, and shrinkage of the network. Four processes are included in the aging process: polymerization, syneresis, maturation, and phase transformation [Hess93].

These processes can occur singly or simultaneously.

The polymerization process involves condensation reactions that increase cross-linking in the gel structure [Hess93, Hess95]:



In some gels (silica gel), polycondensation continues to occur after gelation due to the large concentration of silanol groups [Hess93, Hess95]. Further hydrolysis to re-equilibrate reactions can also occur during aging. The re-equilibration reaction is the reverse of the hydrolysis reaction [Hess95]:



Re-equilibration reaction can be suppressed by using anhydrous water.

Syneresis can be defined as the shrinkage that takes place during aging as a result of condensation reactions [Hess95]. Gel shrinkage is accompanied by expulsion of pore liquid. The formation of bridging bonds by polycondensation causes syneresis [Hess95]. As the formation of bridging bonds proceeds, the contraction of the gel increases. The syneresis mechanism in particulate gels is somewhat different than that previously described. Gelation in particulate gels occurs as a result of the collapse of the electrical double layer, and Van der Waals attraction forces resulting in syneresis [Hess95].

Coarsening, or ripening, is a process by which dissolution and re-precipitation occur as a result of the solubility differences, S , between surfaces with different radii of curvature [Ric88]. Convex surfaces (which have positive radii of curvature) are more soluble than concave surfaces (negative radii) [Hess8, Lin90]. When a gel is immersed in a liquid in which it is soluble, dissolution occurs at the convex surfaces and re-precipitation occurs at the concave surfaces. That means that curved surfaces dissolve and defects grow between particles. As a result of the smoothing process, small particles disappear, and small pores are filled in. Neck growth provides the network with higher strength and stiffness.

After coarsening, the gel has a larger average pore size and a smaller surface area [Ric79]. The larger pore size results because the stiffer gel produced by aging does not shrink significantly under the capillary pressure [Ric88]. The reduction in the surface area is a result of the *dissolution/re-precipitation* process. Coarsening does not result in shrinkage, as the centers of the particles do not move toward each other. The rate of ripening is controlled by temperature, pH, concentration, and type of solvent.

Several types of phase transformations can occur during aging. These include interdiffusion and segregation. Microsegregation is a solid/liquid phase separation that occurs on a local level. This phase transformation is driven by the affinity of the polymer for itself rather than the liquid. Segregation occurs when the liquid separates into two distinct phases. For example, the presence of an unreacted metal sulfide in an isolated region within the pure liquid.

CrySTALLINITY is also observed in aged gels [Bar90]. Although most gels and prepolymers are amorphous, aging permits the structure to rearrange by dissolution and re-precipitation, resulting in crystalline products. Crystallization can be accelerated under certain hydrothermal conditions.

Drying

Drying is the process of removing liquids such as alcohols and water from the gel [Bar89]. Drying under normal conditions gives rise to capillary forces which result in shrinkage of the gel [Bar89]. The resulting product is referred to as a xerogel [Bar89, Jac89]. When drying is carried out under hypercritical conditions, shrinkage does not occur and the resulting gel has a high surface area. This type of gel is referred to as an aerogel [Bar89]. Only drying under normal conditions is considered in this section. Drying can be divided into three stages: constant rate stage, first falling rate, and second falling stage.

Constant rate stage

In the constant rate stage, evaporation rate per unit area is independent of time. During this stage, the gel shrinks by an amount equal to the volume of liquid evaporated, and the liquid-vapor interface remains at the outer surface of the gel. As capillary forces affect the behavior of the gel during this stage, a brief discussion of relevant parameters follows.

If the solid-vapor interfacial energy, γ_{sv} , is higher than the liquid-vapor interfacial energy, γ_{lv} , the liquid tends to cover the solid surface and eliminate the solid-vapor interface [Ruf93]. The change in energy produced by spreading the liquid film is [Ruf93]

$$\Delta E = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} \quad (3.36)$$

where γ_{sl} is the liquid-vapor interfacial energy. If $\Delta E < 0$, the liquid will spread spontaneously to reduce the energy of the system.

The condition for minimum energy can be specified using the contact angle. The contact angle, θ , is the angle between the solid surface and the tangent to the liquid surface at the contact point. The interfacial energies are related to the contact angle by the equation [Ruf93]

$$\gamma_{sv} \cos \theta = \gamma_{lv} - \gamma_{sl} \quad (3.37)$$

When $\theta > 90^\circ$, wetting condition occurs in which liquid is depressed in the capillary. When $\theta = 90^\circ$, wetting occurs and the liquid is elevated in the capillary. When $\theta = 0^\circ$, spreading occurs and the liquid covers the solid surface completely.

Liquid rises in a capillary tube to replace the solid-vapor interface with a solid-liquid interface [Ruf93]. The liquid rise results in an energy gain of $2\pi r h(\gamma_{sv} - \gamma_{sl})$, where r is the tube radius and h is the height to which the liquid rises. The work done by the liquid against gravity is equal to the product of the capillary pressure, P_c , and the volume of liquid moved, $\Delta V = \pi r^2 h$. By equating the energy gained to the work done, the capillary pressure can be calculated [Ruf93]

$$P_{\text{cr}} = \frac{2\gamma_{\text{SL}}\cos\theta}{r} - \frac{2\gamma_{\text{LV}}\cos\theta}{r} \quad 1.38$$

where the negative sign indicates that the liquid is in tension.

Defining the radius of meniscus as [Bir90]

$$r = \frac{R}{\cos\theta} \quad 1.39$$

the capillary pressure becomes

$$P_{\text{cr}} = -2\frac{\gamma_{\text{LV}}}{r} \quad 1.40$$

The gas network support the stress in the liquid, and as a result, is placed in compression. Since alcohol-derived gels have compliant networks, the compressive force causes these networks to contract into the liquid [Bir90]. Initially, the capillary pressure is low, and the radius of meniscus is much larger than the pore radius. As drying continues, the network stiffness increases due to the formation of new bonds and the decrease in porosity. As a result of the increased stiffness of the network, the tension in the liquid rises.

The end of the constant rate stage occurs when the radius of the meniscus becomes equal to the pore radius. This critical or "bottleneck" point occurs when the liquid exerts the maximum force on the pore wall [Bir90, Bir90]. Past the critical point, the tension in the pore liquid cannot overcome further stiffening of the network. As a result, the meniscus withdraws into the pores leaving air-filled pores near the outside surface of the gel. Therefore, during the constant rate stage, the

meniscus recedes at the outside surface, and the meniscus radius decreases continuously.

The first falling stage

During the first falling stage, the evaporation rate per unit area decreases with time [Be79]. The second stage begins when shrinkage ceases due to the increase in the wetness of the gel. During this step, the liquid wedges into the interior and remains in the lamellar condition, leaving air-filled pores near the surface. However, evaporation from the outside surface continues due to the presence of a continuous liquid film that supports flow in the interior. The presence of adjacent pathways allows flow of liquid to occur.

Liquid flow in the first falling stage is driven by a capillary pressure gradient that is a result of a vapor pressure gradient within the pore. The liquid in the lamellar state flows toward the exterior where evaporation occurs. Evaporation occurs at the outside surface because the vapor pressure is lower than it is at the inside of the pore. For a given vapor pressure, all menisci have the same curvature. Therefore, when gels contain variable pore sizes, larger pores empty first [Be79]. If the large pores are interconnected, regions of drained pores will present. These regions may be large enough to scatter light, resulting in an opaque gel [Slee90 and Be79]. These opaque gels are usually clear when fully saturated or fully dried. The presence of variable pore sizes can also result in cracking during drying due to the development of differential stresses [Slee90].

The second falling stage

In the stage isolated liquid pockets are formed, i.e. liquid leaves the granular condense, and drying continues by evaporation of the liquid within the body and diffusion of the vapor to the outside [Birk6]. The drying front is characterized by a flow of liquid from the fibrous region which evaporates at the boundary of fibrous granular regions.

The isolated liquid pockets have a high capillary pressure, but do not exert a significant force on the solid network because they occupy a small volume fraction. As drying continues, the saturated region withdraws into the body, which in turn depends on the total stress as the network is relieved. As a result of the network being compressed more in the saturated region than near the drying surface, differential stress increases.

The development of a differential stress causes warping if only one side is being dried. This warping is permanent, which indicates that the unsaturated region of the gel retains some plasticity during the second falling rate stage. As the saturated region thickness decreases, its contraction is more effectively prevented by the larger unsaturated region. The resistance the saturated region encounters to contract increases the local network tension. This phenomenon accounts for the observed formation of cracks near the drying surface [Birk6].

Dehydration

The dehydration process involves the removal of physically adsorbed water (physorbed water) and chemically adsorbed water (chemisorbed water) [Hos94]. Physorbed water is bound to the gel surface, while chemisorbed water is hydroxyl groups associated with the gel surface. If the physorbed and chemisorbed water are not removed completely, poor optical properties or bloating during sintering can result [Hos90, Bar90].

Thermal dehydration

In thermal dehydration, hydroxyl (OH) groups are removed through a condensation reaction that is carried out at elevated temperatures. The rate of dehydration is a function of temperature and the concentration of remaining OH groups [Re77]. Physorbed water is removed first at low temperatures, followed by the removal of weakly hydrogen bonded OH groups. As the dehydration process proceeds, strongly bonded OH groups are removed, and finally, removal of isolated OH groups takes place. Removal of isolated OH groups occurs at high temperatures because diffusion of protons is required for condensation to take place [Re90]. For systems that sinter at low temperatures, thermal dehydration is often not sufficient to avoid bloating, some densification begins before the complete removal of OH groups.

Ramulative thermal dehydration can be achieved by optimizing the gel microstructure and the thermal processing conditions [Re90]. Pore size, surface area,

and curvature are among the important microstructural variables that affect dehydration. Dehydration can be improved by increasing the pore size. Larger pores enhance the diffusion of the condensation by product, H_2O , and hamper sintering. Consequently, large pores permit complete dehydration to occur before pore closure.

High surface curvature are achieved by releasing processing conditions that result in particulate rather than a polymeric microstructure [BeVO]. Particulate microstructures possess porous structures that facilitate dehydration due to reduced hydrogen bonding. Also, the low surface area to volume ratio associated with particulate microstructures leads to faster dehydration due to a reduced OH concentration on a per-pore basis. Large particles are advantageous from the stand point of surface area to volume ratio and negative radii area. Large particles have low surface area to volume ratio and low negative radii surface area. On the other hand, large particles possess smaller curvature which can result in slower dehydration.

Chemical dehydration

Thermal dehydration normally does not reduce the [OH] sufficiently for optical applications (i.e., optical materials) [BeVO]. Consequently, finding another dehydration technique is necessary in order to achieve low OH content. Chemical dehydration has been investigated as a method to produce low OH content. This process employs the reaction between halogens and OH groups to dehydrate the surface.

Hair et al. investigated chemical dehydration of silica surface by replacing hydroxyl groups with chlorine atoms in a process referred to as chlorination [146b]. Chlorination can be achieved by using Cl_2 gas. Chlorination using this method does not take place at temperatures $< 300^\circ\text{C}$.



Chlorination of silica gel can also be carried out by using thionyl chloride (SOCl_2) [146c].



Although virtually complete dehydration of silica surface can be produced by chlorine treatment, leaching can occur when heating in the vicinity of the refluxing point [146d]. This leaching is a result of chlorine evolution as it replaces the OH groups during the dehydration process. Therefore, a dechlorination treatment (process to remove surface chlorine) is necessary to prevent leaching. In regions of incomplete chlorination, Cl may be removed by the following reaction [146d]:



Dechlorination can be carried out by heating below the refluxing temperature in dry oxygen environment [146d]. This oxidation treatment is diffusion controlled, and can result in a significant decrease in chlorine.

Since the chlorine content is proportional to the surface area of the gel, reduction of surface area prior to the chlorination treatment can result in a lower

reacted chlorine content [Burl4]. Gels can be pre-cured in order to reduce surface area. The degree of pre-curing is controlled so that no closed pores are developed. The development of closed pores hinders the delignification process.

Foaming can also be eliminated by using fluorine instead of chlorine [Burke]. Fluorine can be introduced as HF , NH_4F , or SF_6 , and can replace Cl groups in a manner similar to Cl [Burke].



Foaming does not occur when using fluorine due to stronger Si-F bonds. However, fluorine is retained in the final gel.

Sintering

Sintering is a densification process that is driven by the tendency to decrease the surface area in order to reduce the surface free energy of the material [Kish and Burke]. The surface free energy is reduced by the elimination of the solid-vapor interface. Gels generally have large surface areas, resulting in a relatively high driving force for sintering. The high driving force produces sintering at exceptionally low temperatures, where the transport processes are slow. Amorphous materials sinter by viscous flow, while crystalline materials sinter by solid-state diffusion [Burke]. One of the important aspects on changes and solid-state sintering is the effect of surface curvature on vapor pressure over the surface. This vapor pressure difference has an important role in the material transfer during sintering.

The pressure difference across a curved surface can be determined by considering a bubble being blown in a liquid bath by a capillary (Klotz). If the gravitational effect is negligible, the only resistance to expansion of the bubble is the increased surface energy that is caused by the increase in the surface area. During equilibrium, the following equation must hold (Klotz)

$$\Delta P \cdot v = \sigma \cdot dA \quad (3-45)$$

where ΔP = the pressure difference across the curved surface, v = volume per unit area. The left hand side of the equation 3-45 represents the work of expansion, and the right hand side represents the increased surface energy. The values of dv and dA with respect to the radius of curvature, r , are (Klotz)

$$dv = 4\pi r^2 dr \quad (3-46)$$

$$dA = 8\pi r dr \quad (3-47)$$

Substituting the values of dv and dA in equation 3-45 results

$$\Delta P = \sigma \left(\frac{2}{r} \right) \quad (3-48)$$

Equation 3-48 is valid for spherical shapes. For more general shapes (Klotz)

$$\Delta P = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (3-49)$$

where r_1 and r_2 are the principal radii of curvature

The increase in vapor pressure due to an applied pressure of ΔP can be calculated from (Klotz)

$$V\Delta P = RT\ln\left(\frac{p}{p_0}\right)\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \quad 3.50$$

where V = molar volume, p = vapor pressure over the curved surface, p_0 = vapor pressure over a flat surface, and R = gas constant. Rearranging equation 3.50

$$\ln\left(\frac{p}{p_0}\right) = \frac{M\gamma}{pRT}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \quad 3.51$$

where M = molecular weight, ρ = density, and T = temperature. Equation 3.51 relates the difference in the vapor pressure to the curvature, and is called Thompson-Freundlich (Kelvin) equation.

Vacuum sintering of amorphous materials

The driving force for vacuum sintering is a lowering of the surface energy by reducing the surface area. Considering the neckgrowth of a pair of spheres, Frankel derived a model for vacuum sintering [Katz and Rosin]. When two spherical particles in contact, there is a negative pressure at the small negative radius of curvature of the contact area (r) compared to the surface of the particle. This pressure difference causes a vacuum flow of material to the neck region.

During vacuum flow sintering, the neck widens and the corners of the particles approach one another causing shrinkage. The rate of growth of the neck area was obtained by Frankel [Katz, Kurtz, Rosin and Frankel]

$$\frac{r_1}{r_2} = \left(\frac{3\gamma M}{2\rho RT}\right)^{\frac{1}{2}} \left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad 3.52$$

where r_n = neck radius, r_p = particle radius, γ_{sv} = solid-vapor interfacial energy, v = viscosity, and t = time. This relation was verified experimentally by Kinsinger, Kinsinger, and Song (Kinsig and Kinsig). The increase in the neck diameter is proportional to the square root of time. The rate determining factors for this process are surface tension, viscosity and particle radius. Higher sintering rates are achieved when the particle size and viscosity are small and surface tension is large.

The processing temperature has an important effect on the sintering rate. The sintering rate is proportional to γ_{sv}/η . A change in the temperature results in changes in the content of the surface OH groups, and consequently, in the surface energy [Br90]. However, the loss of OH occurs over a wide range of temperatures. Over the same range of temperatures, the viscosity changes by many orders of magnitude. As a result, the temperature dependence of the sintering rate is governed entirely by the viscosity [Br90].

At low temperatures, the viscosity of glasses is represented by (Zurfi, Br90)

$$\eta = \eta_0 \exp\left(\frac{A G}{RT}\right) \quad (1.13)$$

where $A G$ = activation energy for viscous flow, k = Boltzmann's constant, T = temperature, and η_0 can be calculated from (Zurfi)

$$\eta_0 = \frac{kT}{V_m} \quad (1.14)$$

where η is a frequency factor, and V_m is the volume occupied by a molecule. Equation 1.13 leads to an Arrhenius dependence for the viscosity (Zurfi).

$$\log \eta - \log A + \frac{B}{T} \quad (3.55)$$

where A and B are constants.

At high temperatures, the viscosity of glass departs from Arrhenius behavior to follow what is called Vogel-Poolzer-Thomas empirical equation [Zee93, Eyr93]

$$\log \eta - \log A_1 + \frac{B_1}{T - T_0} \quad (3.56)$$

where A_1 , B_1 , and T_0 are constants.

Kempy and Burg developed a procedure to derive the shrinkage rate [Kie85]

Considering the volume of the neck region [Kie85]

$$V_c = \frac{\pi R^3}{3} \quad (3.57)$$

Substituting equation 3.52 in 3.57 results in

$$V_c = \frac{9\pi a^3 \gamma^3}{16} \quad (3.58)$$

Taking the derivative of V_c with respect to t

$$\frac{dV_c}{dt} = -\frac{18\pi a^3 \gamma^3}{16} \quad (3.59)$$

where the negative sign indicates the decrease in volume. The volume decrease at the sphere at each contact is [Kie85]

$$\frac{dV_s}{V_s dt} = -\frac{2\pi \gamma^3}{16 a^3 \gamma^3} \quad (3.60)$$

where V_0 is the initial volume of the sphere. Considering each sphere has a number of contacts $= n$, and by integrating equation 3-68 [Kin55]

$$\frac{\Delta F}{V_0} = \frac{2\pi\eta\dot{\gamma}^2}{16r^3\eta_0^2} \quad (3.69)$$

Equation 3.69 represents the shrinkage rate during viscous flow sintering. The expression is expected to hold in a volume shrinkage of 2% with reasonable precision.

Sintering of crystalline materials

As with viscous flow sintering of amorphous materials, sintering of crystalline materials is driven by the tendency to lower the surface free energy by reducing the surface area [Birk0 and Kin76]. The surface free energy is reduced by replacing the high-energy solid-vapor interface by a lower energy solid-solid interface. Material transfer during sintering of crystalline materials is influenced by the pressure difference and changes in free energy across a curved surface.

Evaporation-condensation and solid-state diffusion are the mechanisms by which material can be transported in a crystalline material. Evaporation-condensation and solid-state diffusion paths are illustrated in Figure 3-5. Material transport by solid state diffusion is divided into the following mechanisms [Kin76, Birk0]



Figure 3-1 Water transport paths during solid-state sintering. 1) Surface diffusion; 2) Lattice diffusion from the neck; 3) Vapor transport; 4) Boundary diffusion; 5) Lattice diffusion from the grain boundaries and 6) Lattice diffusion from the neck. Adapted from [Rat74]

- Surface diffusion is which the surface is the source and the path of the transported material.
- Lattice diffusion is which the surface, grain boundary, or dislocation is the source and the surface is the path
- Grain boundary diffusion is which the grain boundary is the source and the path of the transported material

Evaporation-condensation mechanism

In the evaporation-condensation mechanism, material is transported from the region of high vapor pressure (the particle surface) to the region of low pressure (the neck). The evaporation-condensation process results in a decrease in the energy of the system, but it does not produce densification [Kins93]. Changes in pore-shape are produced during this process, but shrinkage does not occur.

In order to determine the growth rate of the neck between two particles, consider the Thomson-Freundlich equation for two bonded particles [Kins93, Kins96]

$$\ln \frac{P_1}{P_2} = \frac{2\gamma M_p}{\rho R T} \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \quad 3.42$$

where P_1 is the pressure over the small radius of curvature of the neck. The pressure difference $P_2 - P_1$ is small, and $r_2 \gg r_1$. As a result, to a good approximation, $\ln P_1/P_2 \approx \Delta P/P_2$, and equation 3.42 becomes [Kins93]

$$\Delta p = \frac{\gamma M_p}{r_p kT} \quad (3.43)$$

where Δp is the difference between the vapor pressure of the small, negatively curved surface and the vapor pressure over the nearly flat particle surface.

Using the Langmuir equation for the rate of material transfer, \dot{m} (Kin53)

$$\dot{m} = \alpha A_p \left(\frac{M}{2\pi kT} \right)^{1/2} \quad (3.44)$$

where α is an accommodation coefficient that is approximately equal to 1. The rate of condensation is equal to the volume increase (Kin53):

$$r_p \frac{dV}{dt} = \frac{\dot{m}}{\rho} \quad (3.45)$$

From the geometry of the two spheres in contact, Figure 3-2, $a = r_p^2/2r$, $A = \pi^2 r_p^2/r$, and $v = m_p^3/3r$. Substituting values for m , A , and v in equation 3.45 and integrating, the relationship for the rate of growth of the bond area between particles is obtained (Kin55, Kin'56)

$$\frac{r_p}{r_p^2} = \frac{2\gamma G M^2 m_p^2}{\rho k T^2} \left[\frac{1}{r} - \frac{1}{r_0} \right] \quad (3.46)$$

In addition to time, the main variables that affect the rate of pore-shape change through this process are the particle radius and the vapor pressure. The vapor pressure increases exponentially with temperature, resulting in a strong dependency of evaporation-condensation process on temperature (Kin'56)



Figure 3-2. Schematic of the initial stages of clustering by evaporation/condensation mechanism. Adapted from [Kuc55]

Solid state mechanisms

The difference in the free energy between the neck area and the surface of the particle provides the driving force for material transfer (Kle76). Matter can move from the surface, from the grain boundary, or from the bulk by surface, grain boundary, or lattice diffusion. Similar to evaporation-condensation, the transfer of material from the surface to the neck by surface or lattice diffusion does not lead to shrinkage or densification (Br76) and (Kle76). Shrinkage and densification take place when material is transported from the particle volume or from the grain boundary between particles.

Considering the case of matter transport from the grain boundary to the neck by lattice diffusion, and from the geometry of the neck region as shown in Figure 3.3, the following is obtained (Kle83):

$$F = \gamma_p \frac{1}{2} \pi a, \quad V = \pi r_n^2 / 2r \quad 3.67$$

The surface energy produces an excess of vacancies in the regions of negative curvature (Br76). This excess of vacancies results in a flux of vacancies away from the perimeter of the neck. The vacancy flux per unit time per unit length, J , can be written as follows (Kle75):

$$J = -D_v \Delta N \quad 3.68$$

where D_v = vacancy diffusion constant, ΔN = the excess concentration of vacancies. The excess concentration of vacancies is determined from (Kle75):



Figure 3-3 Schematic of small-scale solid-state winding. Adapted from [Kuo00]

$$\Delta R = \frac{4\pi r^2 D}{A} \quad (3.68)$$

where a = atomic radius, and N_s = vacancy concentration at a phase surface. The self-diffusion coefficient is related by [Kard5]:

$$D_s = a^2 D_v N_s \quad (3.69)$$

Also, the rate of volume change, dV/dt , is related to the vacancy current, \dot{N} , by [Kard5]

$$\frac{dV}{dt} = 3a\omega_v \rho^2 \dot{N} \quad (3.70)$$

Substituting equations 3.68, 3.70, and 3.71 into equation 3.66 and integrating yields the neck growth rate [Kard5]

$$\frac{r_0}{r_1} = \left(\frac{48\pi a^2 D_s}{A} \right)^{\frac{1}{3}} \left(\frac{t}{t_0} \right)^{\frac{2}{3}} \quad (3.72)$$

The shrinkage rate is determined through the same procedure that was used for vacuum sintering [Kard5]

$$P_1 r_0^2 \left(\frac{48\pi a^2 D_s}{A} \right)^{\frac{1}{3}} \left(\frac{t}{t_0} \right)^{\frac{2}{3}} \quad (3.73)$$

and

$$\frac{\Delta V}{V_0} = -\frac{2a\omega_v}{3} \left(\frac{48\pi a^2 D_s}{r^2 A} \right)^{\frac{1}{3}} \left(\frac{t}{t_0} \right)^{\frac{2}{3}} \quad (3.74)$$

Equation 3.74 is reported to hold to a volume shrinkage of 25%

Equations 3.32 and 3.34 indicate that the neck growth rate is proportional to $r^{1/2}$, and that the shrinkage rate is proportional to $r^{3/2}$ [Kus96]. Control of particle size is important, since the sintering rate is roughly proportional to the inverse of the particle radius. This means that as the particle size is increased, the sintering rate is decreased.

The mobility of atoms is high within the grain boundary. Consequently, diffusion in the grain boundary is rapid. However, the flux of diffusing atoms is small because the grain boundary cross-sectional area is very small [Br90]. Diffusion through the lattice, on the other hand, is very slow, but the flux can pass through a larger area. As a result, the net rate of transport by lattice diffusion may be greater than that of grain boundary diffusion.

The particle size can determine which transport mechanism is dominant. Grain boundary diffusion is dominant in case of small grains due to the large volume fraction occupied by the grain boundary. The activation energy for lattice diffusion is higher than that of grain boundary diffusion [Br90]. However, the lattice diffusion coefficient increases rapidly with temperature. As a result, lattice diffusion becomes more important at high temperatures. It has been observed that surface diffusion is most important during the early stages of sintering. This diffusion affects the neck diameter but not the shrinkage or porosity [Kin96]. Grain boundary and lattice diffusion become important following the early stages of sintering.

As shown in equations 3.41 and 3.39, the sintering rate is proportional to r^2 for vacuum sintering, and is proportional to $r^{4/3}$ for lattice or volume diffusion. This

means that viscous flow sintering is much faster than solid-state diffusion sintering. The difference in the sintering rate for the two mechanisms can have significant effects on the densification behavior of some systems. Rader and Pank reported very rapid densification in alumosilicates with compositions that contained large amounts of liquid phase [20c]. High densification rates persisted up to an alumina content of 74 wt%, at which a sharp decrease in the densification rate was observed. This sharp decrease in densification rate occurred at the transition from multi-phase region to a single alumina region. This transition was associated with the elimination of the glass phase. The drop in the densification rate was attributed to absence of viscous sintering and the activation of solid-state sintering.

CHAPTER 4 COMPOSITE MATERIALS

Definitions and Characteristics

Composites are materials that consist of two or more chemically and physically distinct constituents on a macroscopic level [Agar03, Hull87]. Composites can be made by joining the separate constituents in such a way that the dependence of one constituent on the other can be done in a controlled way to optimize properties. Since the constituents may be individually tailored to enhance separate physical or chemical characteristics, the properties of the composite should be superior to those of the individual components. Composites consist of one or more discontinuous phases, called the reinforcing material, embedded in a continuous phase, called the matrix. In general, reinforcing materials are stronger and harder than the matrix.

Properties of composites are highly dependent on the properties of their constituent materials. The properties of composites are also influenced by the distribution of the constituents and the interaction among them [Agar03]. These properties may be the volume fraction sum of the properties of the constituents, or the properties of the composite work together to provide properties that are not accounted for by the volume fraction sum of the constituents' properties. Composites can be described by the geometry of the reinforcement. The geometry of the reinforcement is described by size, shape, and size distribution. Composites with

identical reinforcement geometry may differ in concentration, orientation distribution, and arrangement.

Concentration is considered the most important parameter influencing the composite properties [AguiR]. It is considered an uncontrollable manufacturing variable used to dictate the properties of the composite. The concentration distribution can be used to determine the homogeneity of the composite material system [AguiR]. Particles may be uniformly dispersed in a composite without touching each other. Particles can also be arranged in a way to form a network with a continuous path connecting all particles.

The orientation of the reinforcement has a great influence on the anisotropy of the system [AguiR]. In the case of spherical reinforcement particles, the composite behaves as an isotropic material. For reinforcement particles with unequal dimensions, anisotropy is obtained if they are randomly oriented, an example is the randomly oriented, short-fiber reinforced composite. In some cases, anisotropy is desired in order to improve a certain property in a specific direction. Continuous-fiber-reinforced composites can be anisotropic, if the fibers are aligned in one direction or woven in stacked phases. Anisotropy can also be introduced by using certain manufacturing processes, such as extrusion of short-fiber composites.

The majority of structural composites have been fabricated to improve the mechanical properties, such as strength, toughness, stiffness, and high-temperature performance [AguiR]. The geometry of the reinforcement has a strong influence on the strengthening mechanism. Consequently, reinforcement phase geometry can be

considered as a basis for classification of composites. Composites can be divided into two major categories [Agar10]. The first category is called particle-reinforced composites (*particle-reinforced composites*). This category includes all composites with particles that are nonfibrous in nature. The particles may be spherical, plate-like-shaped, cubic, triangular, or any other regular or irregular shape that is approximately equiaxed. The second category consists of fiber-reinforced composites (*fiber-reinforced composites*). A fiber is distinguished by its length being much greater than its cross-sectional dimensions [Agar10]. The emphasis in this study is on unidirectional fiber composites; other composites are beyond the scope of this study.

Unidirectional Fiber Composites

Unidirectional fiber composites contain fibers that are aligned parallel to each other in a single direction. These composites have two important features; their high strength-to-weight ratio, and controlled anisotropy [Agar10]. Unidirectional fiber composites are divided into *discontinuous (short) fiber-reinforced composites* and *continuous-fiber unidirectional composites*. In *discontinuous-fiber unidirectional composites* the fiber cross-section cannot be controlled easily. In these composites the load-bearing capability is a function of the fiber length.

Continuous-fiber composites have a higher strength and modulus values in the direction of the fiber axis than the strength and modulus of short-fiber composites [Agar10]. However, these composites are very weak in the transverse direction.

Therefore, continuous-fiber composites are superior to short-fiber composites when load is applied in the longitudinal direction (parallel to fibers).

The use of fibers in high performance engineering materials is based on the following characteristics [Chall7]:

- A high aspect ratio (length (L)/diameter (ϕ)) that facilitates the transfer of a major part of the applied load by the matrix to strong fibers.
- A small fiber diameter with respect to grain size. This allows a higher fraction of the theoretical strength to be attained than that possible in a bulk form, because the smaller size has a lower probability of having large surface flaws.
- A high degree of flexibility that is a characteristic of a material with high modulus and small diameter. The flexibility allows a variety of techniques to be used in manufacturing composites with these fibers.

Unidirectional composites consist of parallel short or continuous fibers embedded in a matrix. Several unidirectional layers (which referred to as a lamina) can be in a specified orientation, to form a laminate [Py93, Agr93]. Figure 4-1 shows a continuous-fiber composite laminate. Laminates are considered building blocks that are used to make high performance structural elements. Since the main application of unidirectional composites is for load bearing, understanding the mechanics of these composites is essential.

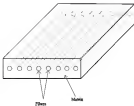


Figure 4-1 Unidirectional continuous-fiber composite lamina. Adapted from [Ag80].

Mechanism of Fiber Composites

Designing composites to sustain high loads for various applications requires a thorough understanding of composite mechanics. The behavior of unidirectional composites is a result of the behavior of the interface between the fiber and the matrix, and the behavior of the fiber and the matrix themselves [Choi7].

The fiber interface is responsible for transmitting the load from the matrix to the fiber [Ayoub]. The fibers constitute the greater portion of the composite strength. This means that the efficiency of load transmission from the matrix to the fibers can have a large influence on the strength of the composite. There are two types of bonding that can exist at the fiber-matrix interface, mechanical bonding and chemical bonding [Choi7]. Mechanical bonding can occur by simple mechanical locking effects between two materials. The mechanical locking can be produced by having a rough fiber-matrix interface. It can also be produced by the contraction of the matrix against the fibers. In most cases, mechanical bonding alone is not enough to have an effective reinforcement. However mechanical bonding can add to the overall bonding, in the presence of reaction bonding.

Chemical bonding can be divided into two types, dissolution and wetting/bonding, and reaction bonding [Choi7]. In dissolution and wetting/bonding, interaction between components occurs at an electronic scale. The bond strength varies from weak Van der Waals to strong covalent bonds. Intimate contact is required between the fiber and the matrix to achieve this kind of bonding, also

these interactions are short range. This implies that no constraints on the fiber surface, or entrapped air or gas bubbles at the interface, should be allowed to exist.

Reaction bonding occurs by transport of atoms from the fiber and the matrix to the interface, which is considered the reaction site [Chall7]. The reaction products and the reaction rates depend on the matrix composition, reaction time, and temperature. The kinetics of the surface reaction rate \dot{x} is generally described by the formula [Chall7]

$$\dot{x} \propto \sqrt{Dt} \quad (4.1)$$

where D = diffusion coefficient, t = time. The diffusion coefficient is determined by the formula [Chall7]

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (4.2)$$

where D_0 = constant, Q = activation energy, k = Boltzmann constant, and T = temperature.

Modeling of Unidirectional Continuous Fiber Composites

Consider the case of a continuous-fiber composite with parallel fibers under a longitudinal tensile load. Assuming a perfect fiber to matrix bonding, the longitudinal stress in fibers (σ_f), matrix (σ_m), and composite (σ_c) are equal [Agall and Mall8]

$$\varepsilon_f = \varepsilon_m = \varepsilon \quad (4.3)$$

From linear elasticity theory, the stress and the strain are proportional to each other according to Hooke's law [Tim70]:

$$\sigma = E\varepsilon \quad (4.4)$$

where σ is the stress, which is the amount of load applied per unit area, and E is Young's elastic modulus. Assuming both fibers and matrix behave as linearly elastic materials [Mal88]:

$$\sigma_f = E_f \varepsilon_f = E_f \varepsilon \quad (4.5)$$

$$\sigma_m = E_m \varepsilon_m = E_m \varepsilon \quad (4.6)$$

where σ_f = fiber stress, σ_m = matrix stress, E_f = fiber elastic modulus, and E_m = matrix elastic modulus.

The tensile load applied on the lamina, P_x , is shared by the matrix and the fibers [Mal88]:

$$P_x = P_f + P_m \quad (4.7)$$

where P_f = load applied on fibers, and P_m = load applied on matrix. Using the definition of stress, equation 4.7 becomes [Agi98] and [Mal88]:

$$\sigma_f = \sigma_f \frac{A_f}{A_x} = \sigma_m \frac{A_m}{A_x} \quad (4.8)$$

where σ_x = average tensile stress in the lamina, A_f = net cross-sectional area for fibers, A_m = net cross-sectional area for matrix, A_x = cross-sectional area of the

composite, i.e. $A_0 = A_f + A_m$. Defining fiber and matrix volume fractions [Agar0 and Mull8]:

$$V_f = \frac{A_f}{A_0} \quad (4.9)$$

$$V_m = \frac{A_m}{A_0} \quad (4.10)$$

Then equation 4.8 becomes [Agar0]:

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \quad (4.11)$$

or

$$\sigma_c = \sigma_f V_f + \sigma_m (1 - V_f) \quad (4.12)$$

Dividing equation 4.11 by the stress value [Mull8]:

$$E_c = E_f V_f + E_m (1 - V_f) \quad (4.13)$$

where E_c = average composite elastic modulus. Equations 4.12 and 4.13 indicate that the contributions of the fibers and the matrix to the average properties of the composite are proportional to their volume fraction. Both a relationship is referred to as the rule of mixture [Agar0 and Mull8].

The fraction of load-carryed by the fibers in a unidirectional continuous fiber lamina can be determined by dividing the load applied to the fibers by the load applied to the composite [Mull8]:

$$\frac{F_f}{F_c} = \frac{1}{1 + \frac{E_c}{E_f} \left(\frac{1}{V_f} - 1 \right)} \quad (4.16)$$

Equation 4.16 indicates that in order to attain high stresses in the fibers and thereby use the fibers efficiently, it is necessary for the fibers modulus to be much greater than the matrix modulus [Agallo]. Figure 4.2 shows the fraction of the composite load carried by the fibers. As shown in the figure, the fraction of the total load carried by the fibers increases with the increase in ratio of fiber modulus to matrix modulus and the increase in the volume fraction of fibers. However, when fiber volume fraction exceeds 80%, properties start deteriorating due to the inability of the matrix to adhere the bundles of fibers resulting in poor fiber matrix bonding and void formation in the composite.

Fiber failure strain is generally lower than the matrix failure strain [Malhot]. The brittle rupture of fibers will result in a brittle rupture in the composite. From equation 4.11, the longitudinal tensile strength of a unidirectional continuous fiber composite can be calculated as [Agallo, Hsitt, Mottt]

$$\sigma_{cu} = \sigma_{fu} V_f + C \sigma_{m1} (1 - V_f) \quad (4.17)$$

where σ_{cu} = the longitudinal tensile strength of the composite, σ_{fu} = fiber tensile strength, and $C \sigma_{m1}$ = matrix stress at the fiber failure stress. The strengthening

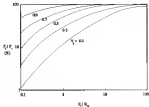


Figure 4.2 Fraction of composite load carried by fibers as a function of fiber modulus/fiber modulus ratio for different fiber volume fractions. Adapted from (Malvern, 1968).

effect is not achieved unless the strength of the composite exceeds that of the matrix alone [Agalló]

$$\sigma_{cm} = \sigma_b F_f + (\sigma_{cm})_0 (1 - F_f) > \sigma_{m0} \quad (4.16)$$

where σ_{m0} = the strength of the matrix. Using equation 4.16, a critical volume fraction of fibers, V_{fc} , is defined [Agalló and Mullis]:

$$F_{fc} = \frac{\sigma_{m0} - (\sigma_{cm})_0}{\sigma_b - (\sigma_{cm})_0} \quad (4.17)$$

This critical volume fraction of fibers has to be exceeded in order for strengthening to occur.

Mechanics of Discontinuous Parallel Fiber Composites

When a load is applied to a discontinuous fiber bundle, it is transferred to the fibers by shear stresses acting at the fiber/matrix interfaces [Mullis]. The lower modulus for the matrix results in the longitudinal strain in the matrix being higher than that in adjacent fibers. As a result, a shear stress distribution across the fiber/matrix interface is established, if perfect fiber-matrix bonding is assumed.

The normal stress distribution in a discontinuous fiber can be calculated by equilibrium analysis. Considering an element with length dx , at a distance, x , from a fiber end (as shown in Figure 4.3), the force equilibrium equation for dx is [Mullis]

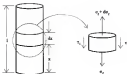


Figure 4-3 Longitudinal tensile loading of a discontinuity that is a mechanical component. Adapted from [96d03].

$$\left(\frac{\pi}{4}d_f^2\right)\left(\sigma_f+\sigma_0\right)+\left(\frac{\pi}{4}d_f^2\sigma_f\right)+\pi d_f\sigma_0x_1 \quad (4.18)$$

where σ_f = longitudinal stress in the fiber at a distance x from one of its ends, σ_0 = shear stress at fiber-matrix interface, d_f = fiber diameter. Equation 4.18 can be simplified to [Malhotra]

$$\frac{d\sigma_f}{dx} = \frac{4\sigma_0}{d_f} \quad (4.19)$$

Ignoring the stress transfer at the fiber ends, and assuming the interfacial shear stress is constant and equal to the matrix yield shear stress, integration of equation 4.19 yields [Malhotra]

$$\sigma_f = \frac{4\sigma_0}{d_f}x \quad (4.20)$$

Equation 4.20 indicates that the fiber stress is not uniform. The fiber stress is zero at the ends and increases linearly to the maximum value at the central portion of the fiber. For short fibers, the maximum fiber stress occurs at $x = L_f/2$, thus [Agarwal and Malhotra]

$$\sigma_{f_{\max}} = 4\sigma_0 \frac{L_f}{d_f} \quad (4.21)$$

"The minimum fiber length in which the maximum fiber stress can be achieved" is referred to as load-transfer length (L_T) [Agarwal]. The load is transferred from the matrix to the fiber over the load-transfer length, which is given by [Agarwal]

$$\frac{L_T}{d_f} = \frac{\sigma_{f_{\max}}}{4\sigma_0} \quad (4.22)$$

Since $\sigma_{f_{\max}}$ is dependent on the applied stress, the load-transfer length is also dependent on the applied stress. A critical fiber length (L_c) can be defined as the

maximum fiber length in which the fiber strength (σ_{f0}) can be achieved [Agar03,Mull88]

$$\frac{E_f \pi r_f^2}{4l} = \pi r_f \sigma_{f0} \quad (4.23)$$

The critical fiber length is independent of applied stress. The maximum value for the load-transfer length is the critical length.

Figure 4-4 shows the significance of the critical fiber length on the longitudinal stresses of the fiber. In the case of fiber length smaller than the critical length, the maximum fiber stress may never reach the value for fiber strength [Mull88]. As a result, either the matrix or the fiber matrix interfacial bond may fail before fibers reach their potential strength. In the case of fiber length equal to the critical length, the maximum fiber stress reach to the fiber strength at the middle of the fiber. The last case is when the fiber length is greater than the critical length, the maximum fiber stress may reach the fiber strength over much of its length. However, the fiber stresses will decay over a distance equal to $L_c/2$ from each end. For effective strengthening, the selected fiber length should be much greater than the critical length.

The average fiber stress can be calculated from the formula [Agar03 and Mull88]

$$\sigma_{f,av} = \frac{1}{L} \int_0^L \sigma_f dx \quad (4.24)$$

The quantity represented by the integral is the area under the curve of fiber stress

Fiber Tensile Strength (σ_{fu})

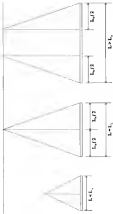


Figure 4-4 Development of initial fiber length on the longitudinal stress of a discontinuous fiber [Majum]

various lengths (Figure 4-5). Therefore, the average fiber stress is [Mads, Ag45B]

$$\sigma_{\text{ave}} = \sigma_{\text{sd}} \left(1 - \frac{L}{L_c} \right) \quad (4.25)$$

In the case of $L = L_c$, equation 4.25 becomes:

$$\sigma_{\text{ave}} = \sigma_{\text{sd}} \left(1 - \frac{L}{L_c} \right) \quad (4.26)$$

and in the case of $L < L_c$, equation 4.25 becomes:

$$\sigma_{\text{ave}} = \frac{\sigma_{\text{sd}}}{2} \quad (4.27)$$

For $L > L_c$, the longitudinal tensile strength of the composite is determined by substituting $L_c = L$ and $\sigma_{\text{sd}} = \sigma_{\text{st}}$ and using the following rule of mixtures [Mads55]:

$$\sigma_c = \sigma_{\text{sd}} F_f + \sigma_{\text{st}} F_m \quad (4.28)$$

Thus, the longitudinal tensile strength of a unidirectional discontinuous-fiber composite is [Ag45B, Hoff1, and Mads55]

$$\sigma_c = \sigma_{\text{sd}} \left(1 - \frac{L}{L_c} \right) F_f + \sigma_{\text{st}} F_m \left(1 - F_f \right) \quad (4.29)$$

For the case of $L = L_c$, equation 4.29 becomes identical to equation 4.13, which is used for continuous fibers. A comparison between equation 4.13 and equation 4.29 shows that continuous fibers always strengthen a matrix more effectively than short fibers.



Figure 4-3. Longitudinal stress distribution along a discontinuous fiber under longitudinal stress testing [Mullis].

In the case of $L < L_{cr}$ no fiber failure occurs. Instead, failure occurs by one of the following failure modes [Mal83]

- Fiber matrix interface bond failure followed by fiber pullout. In this case, the longitudinal tensile strength of the composite is [Mal83]

$$\sigma_{cm} = \tau_{mf} \frac{L}{d} V_f + \sigma_{mf} (1 - V_f) \quad (4.33)$$

where τ_{mf} = shear strength of fiber-matrix interface, σ_{mf} = matrix stress at the instant of fiber pullout.

- Matrix failure, in which the longitudinal tensile strength of the composite is [Mal83]

$$\sigma_{cm} = \tau_{mf} \frac{L}{d} V_f + \sigma_{mf} (1 - V_f) \quad (4.34)$$

where σ_{mf} = tensile strength of the matrix. Which mode is responsible for the failure is dependent on the relative values of τ_{mf} and σ_{mf} .

The discontinuities caused by the presence of fiber ends result in stress concentrations. The stress concentrations are produced because the load that is not carried by the fiber due to the discontinuity must be carried by other fibers. These stress concentrations can have detrimental effect on the strength of the composite.

Failure of Unidirectional Composites Under Longitudinal Tensile Loads

Failure of unidirectional composites that are subjected to longitudinal tensile load is initiated by fiber breakage [Agar8]. Fiber strength in reality is not a single value [Mal83]. Fiber strength follows a statistical distribution due to the presence of defects. Consequently, it is expected that a few fibers will fail at stress levels

below the average strength. The remaining fibers will carry higher stresses, and may not fail simultaneously.

The stress distribution in a fiber changes when breakage occurs. The stress at each of its broken ends becomes zero [Mal83]. However, the stress builds back up to reach the average value over a distance of $l_{av}/2$ from each end. The stress states in the regions of the broken ends contain the following [Mal83]:

- high shear stress concentrations in the matrix within the fiber end region,
- stress concentrations at the void created upon breakage of the fiber, and
- an increase in the normal stress in the neighboring fibers.

The presence of these stresses can result in failure of the composite.

Failure Processes

Fracture toughness of a unidirectional composite is the sum of the energies consumed by several failure processes. These failure processes are fiber debonding, fiber pullout, fiber fracture, and matrix cracking or yielding [Mal83]. An advancing crack always has a longitudinal stress concentration at its tip. The stress component perpendicular to the longitudinal stress, and the shear stress components may reach high values slightly ahead of the crack tip. Depending on the strength of the fiber-matrix interface, these stress components can cause debonding of the fibers from the surrounding matrix by breaking the chemical and secondary bonds between the fibers and the matrix [Agar80, Mal83]. Fiber debonding is more probable to occur than fiber tensile failure when the interfacial bonding is weak and fiber strength is high

A debonding crack may run at the interface or in the adjacent matrix depending on their relative strengths. In both cases, a new surface is created, which results in an increase in the fracture energy.

When a load is applied, fibers start breaking randomly at various locations due to the statistical distribution of surface flaws [Madi]. The opening of the matrix crack causes broken fibers to pull out from the surrounding matrix rather than fibers breaking again in the plane of composite fracture [Agarwal, Madi]. Fiber pullouts occur when brittle or ductile non fibers are used to reinforce a tough matrix. Fiber pullouts occur in the case of fibers whose ends are within a distance of $L_{cr}/2$ of the composite fracture surface. Fiber pullout is opposed by friction at the fiber-matrix interface which results in an increase in the fracture energy. For cases when the fiber length (or broken fiber length) is greater than $L_{cr}/2$ or the interfacial strength is high, fiber failure or fiber debonding occurs first followed by fiber pullout.

The difference between fiber pullout and fiber debonding is that fiber pullout occurs when a crack initiated at the fiber is unable to propagate into the tough matrix, whereas fiber debonding takes place when a matrix crack is unable to propagate across a fiber [Agarwal]. Fiber pullouts are usually accompanied by matrix deformation. In fiber debonding, on the other hand, no matrix deformation takes place. Both mechanisms, fiber debonding and fiber pullouts, significantly enhance fracture energy, and consequently, the toughness of the composite. Figure 4-6 shows fiber debonding and fiber pullouts in a unidirectional carbon-fiber composite.

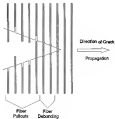


Figure 4-6 Fiber pullout and debonding in a unidirectional continuous fiber composite [Agarwal]

Fibers break when their fracture strain is reached [Agar00]. When a crack propagates in a direction normal to the fibers, fiber failure will eventually take place for complete separation of the laminae. Brittle fibers have low energy-absorbing capability because they have a low fracture strain. Although fibers are responsible for enhancing the strength of the composite, fiber fracture accounts for only a small fraction of the total energy absorbed.

In order for the fracture of the composite to be completed, the matrix material surrounding the fiber has to fracture [Agar00]. Brittle matrices can undergo only a limited deformation, while ductile matrices can undergo extensive plastic deformation. Both cracking and plastic deformation absorb energy. However, the energy required for plastic deformation is much higher than that for cracking. Therefore, the contribution of ductile matrices to the total absorbed energy is significant, whereas the contribution of brittle matrices is relatively insignificant.

CHAPTER 3 EXPERIMENTAL PROCEDURE

Sol-Gel Preparation

Trimethyl orthosilicate (TEOS) was used as a precursor for silica, and aluminum sec-butoxide (ASB) was the precursor for alumina. Two types of solvents were tested for the silica sol, sec-butanol and ethanol, while for alumina sol, only sec-butanol was used as a solvent. It has been observed that there is large difference in the hydrolysis and polycondensation rates between TEOS and ASB [Yoshii]. Hydrolysis and polycondensation rates of ASB is much higher than that for TEOS [Yoshii]. In order to circumvent the difference in the hydrolysis and polycondensation rates, alumina precursor is not generally hydrolyzed prior to mixing with silica sol while, the silica precursor is partially hydrolyzed. A chelating agent was added to the alumina sol to control hydrolysis and to assist in forming a polymeric sol. Two types of chelating agents were used in the process, triethanolamine (TEA) which is an alkylalcohols, and acetylacetone (AcAc) which is a β -diketone.

Figure 3-1 shows the experimental procedure for this study. Alumina sol preparation was done in a controlled environment (drybox) in which the humidity was maintained at very low levels. The controlled environment was needed to prevent the hydrolysis of ASB by humidity. First, the chelating agent and ASB were diluted separately with sec-butanol. Chelating agent/ASB molar ratio (R_1) was varied



Figure 3-1. Flowchart for the experimental procedure

in different experiments. Second, the chelating agent solution was added drop-wise to the ASE solution which was being stirred vigorously. After adding the chelating agent solution, the solution was stirred for 24 hours to ensure homogeneity.

The silica sol was prepared by diluting TEOS in a solvent. A mixture of DI water and solvent was then added to the solution. The water to TEOS molar ratio was 2. The hydrolysis step was carried out by heating the sol to 50°C for 40 minutes in a water bath and was allowed to cool. Finally, the silica sol was added drop-wise to the alumina sol inside the dyke while stirring. The sol mixture (soluble sol) was stored for 24 hours to ensure homogeneity. Solution concentrations were selected to yield an 72-78 wt% alumina/20-25 wt% silica composition after heat treatment. Table 5-1 shows the composition of the different sols used.

The soluble sol was condensed by heating to 30°C-40°C and simultaneously applying a vacuum. Condensation was unattended and the sol was filtered through a 1 micron filter. The filtration step was introduced to remove impurities and, in some cases, precipitates. Precipitates and impurity-free clear sols were required for successful fiber spinning. The sol was further condensed until the rheological conditions for continuous spinnability were achieved.

Fiber Spinning and Aging

The sol with the right rheological conditions was poured into a container inside the spinner. A cup-shaped spinner with 40 µm holes was used. A

Table 3-1. Sample Identification of Bots Used in this Study with Their Competence

Sample ID	Initial Bot Behavior	Challenging Agent	B-Value
STG3	top behavior	TEA	0.3
BT13	middle	TEA	0.3
BT1	middle	TEA	1.0
EAO.3	bottom	AA/AA	0.15
EAO.5	bottom	AA/AA	0.5
EAO.6	bottom	AA/AA	0.6

nitrogen pressure of 1–4 MPa was then applied on the oil inside the sealed spinner. The fibers extruded from the spinner were wound on a rotating drum (brinder) with 15.2 cm diameter. The fiber spinning rate varied between 5.42 m/min and 42.41 m/min. The spinning rate was controlled by the motor speed. A schematic of the fiber spinning assembly is shown in Figure 9B.

After completing the spinning process, the fibers were removed from the drum and were placed inside a 100% humidity chamber for aging. Aging was carried in this study using vapor rather than a liquid. Room temperature and high temperature aging were carried out. The room temperature aging was conducted in a sealed plastic box with water containers inside. High temperature aging was conducted in a sealed furnace with water containers inside. Different aging times and temperatures were tested.

Firing and Characterization

After aging was completed, the fibers were placed on a furnace as an alumina substrate and heated in air. The fibers were heated to 600°C (5°C/min heating rate) and held for 2 hours to remove organics. Following that, the fibers were heated to 900°C (10°C/min heating rate) and held at that temperature for 30 minutes to complete sintering. The fibers were then heated to 1500°C (10°C/min heating rate) and held for 10 minutes to complete crystallization and densification. Other heating schedules were used in different parts of this study.

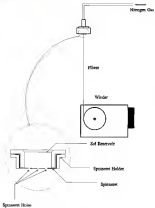


Figure S-2. Schematic of fiber spinning assembly

Various characterization techniques were used in different steps of the process. These include

- Fourier transform-infrared spectroscopy (FT-IR),
- viscosity measurements,
- thermogravimetric analysis/differential thermal analysis (TGA/DTA),
- x-ray diffraction (XRD),
- chemical (acid) etching,
- surface-flux density measurement,
- transmission electron microscopy (TEM),
- scanning electron microscopy (SEM), and
- tensile strength measurement.

The FTIR was used in transmission to detect hydrolytic *in situ* sol (i.e., if silanol groups were present). A rotary viscometer was used to measure the viscosity and shear stress change with shear rate for the molten sol. Viscosity measurements were used to determine sol structure and the conditions for maximum spinnability. Viscosity measurements were also used to determine the effect of different factors (pH value, time, etc.) on sol rheology. Organics removal and surface formation were investigated using TGA/DTA. Determination of the crystalline phases was carried out using XRD. Glass phase detection was carried out by chemically etching fibers. Chemical etching was carried out by immersing the fibers in 5% HF solution for 15 minutes.

Single-fiber density measurements on short fibers were used to determine the densification behavior of fibers. Transmission-electron microscopy was used to detect the presence of intergranular glass phase. Tefel samples were prepared by cutting fibers in an epoxy matrix. The body was cut into thin slices, polished down to 100 microns, then finished further by etching and ion milling.

Scanning electron microscopy was used on short fibers to observe the microstructure of fibers prepared under different conditions. This technique was used in combination with differential etching to determine the presence of a glass phase. It was also used to determine grain growth as a function of time and temperature.

Tensile strength measurements were used to characterize fiber strength after sintering. Single fibers were fixed on a rectangular sheet of paper using wood glue, as shown in Figure 5-8. The center part of the paper was cut out, and the edges were left to hold the sample. After mounting the sample on the tensile test instrument, the paper edges were cut so that the fiber would carry the complete load during the measurement. A gauge length of 1 cm was used for the fibers.



Figure 5-3 Schematic of a small strength test specimen.

CHAPTER 6 RESULTS AND DISCUSSION

Chapter Outline

This chapter describes the experimental investigation into process development for producing continuously spinnable mullicol fibers via the sol-gel process. A discussion of the results of the investigation is presented. The first section deals with the different aspects of the chemical processing of mullicol components with emphasis on the effect of silox pre-spinning hydrolysis on fiber properties.

In the second section, the results of the rheology study are presented. This study investigates the following:

- effect of solvent content and continuous spinning conditions,
- change of rheological conditions with time
- silox sol solvent effect on mullicol rheology
- role of R value.

The third section discusses the TGA/DTA results for various sols. The effect of aging on properties, mullicol formation, and fiber microstructure is discussed in the fourth section. This section also discusses high temperature aging.

The fifth section deals with the densification behavior of fibers and the effect of aging temperature on fiber density. In the sixth and seventh sections, crystalline

phase densitometer and glass plate densitometer results are presented. The eighth section discusses grain growth in molten films as a function of time and temperature. In the ninth section, strength measurement results are presented. In the final section, the results of this study are compared to the results achieved by other investigators.

Chemical Processing of Molten Sol.

The effect of different types of solvents on silica sol characteristics and on the final properties of molten films was investigated. The goal was to determine the effect of pre-solvent hydrolysis of silica sol on the properties of films spun. The two solvents tested were iso-butanol and ethanol. These two solvents were selected because TEOS has different hydrolysis rates in them. When iso-butanol was used as a solvent, no significant hydrolysis was observed. The FT-IR results for silica sol heated at 60°C for 60 min, as shown in Figure 6-1, indicate that hydrolysis did not take place. The associated SiH-OH^2 absorption band which corresponds to the silanol O-H stretching vibration (indicative of hydrolysis) was not observed. Similar results were observed when the silica sol was heated at 60°C for 2 and 4 hr.

The absence of silanol groups had an adverse effect on the formation of the polymeric structure (which is required for film spinning) via polycondensation after mixing with the chlorine sol. The molten sol made from this silica sol was labeled "FSL3". Films drawn from this molten sol had a very poor grain strength. The term "poor grain strength" was used to categorize films that broke into small pieces prior to firing. The term "good grain strength" was used to categorize films which

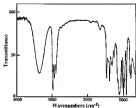


Figure 4-3. FT-IR spectrum for silica sol with iso-butanol solvent heated at 60°C for 60 minutes

maintained integrity before firing. The fibers in which hydrolysis and polycondensation reactions were incomplete were characterized by weak, brittle failure post firing at 1200°C. Poor green strength was a result of the chance of polymer chains. The poor quality of fired fibers was a result of a poorly networked and homogenized green structure.

Figure 4-3 is a SEM micrograph of a fiber made from the STGJ sol with a silica hydrolyzation of 4 hours. As shown in the micrograph, a large whisker-shaped grains and large pores were present. The poor mechanical properties observed for these fibers can be attributed to the microstructure of the fiber, which resulted from the absence of molecular-scale mixing due to the poor hydrolysis of TEOS.

When ethanol (which is normally used in preparing silica sols) was used as a solvent, a pronounced hydrolysis was observed. Results obtained by FTIR for the silica sol heated at 60°C for 60 min showed the presence of the 3075 cm^{-1} absorption band, as shown in Figure 4-3. The formation of silanol groups, as a result of hydrolysis, is essential to the formation of the polymeric structure produced when mixing with titanium sol. A maximum water/TEOS molar ratio of 3 was required to form the desired polymeric structure. A 3-dimensional network structure is produced at higher water/TEOS molar ratios [Sachff]. Molten sols made from this silica sol were labeled "ETGJ". Fibers extruded from this molten sol had good green strength, were flexible, and straight after firing at temperatures above 1200°C.

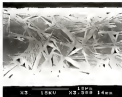


Figure 4-2. SEM micrograph of a fiber made from STG3 gel with silica liquid/sol ratio of 4, fired at 1400°C.

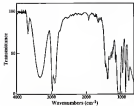


Figure 4-3 FT-IR spectrum for silica gel with ethanol solvent, heated at 60 °C for 60 minutes.

The good glass strength can be explained by considering hydrolysis and polycondensation reactions. The bi-functionality of the partially hydrolyzed TEOS groups (which is a result of using water/TEOS ratio of 1) and the high polycondensation rate of aluminum alkoxide promote the formation of polymeric chains by the polycondensation of partially hydrolyzed chain ends and the unhydrolyzed aluminum moieties. The good characteristics of the fired films were due to the homogeneity obtained from having extensive hydrolysis and polycondensation reactions. Figure 8-4 shows a SEM micrograph of a flexible film made from the ETB-3 sol. The grains were mostly equiaxed and no whisker shape grains were observed.

The difference in the TEOS behavior for the two different solvents can be explained by considering the interchangeability and the hydrolytic resistance of the different alkyl groups. When *tert*-butanol is used as a solvent the following reaction takes place:



The interchangeability of the $(\text{OC}_2\text{H}_5)_3\text{Al}$ is greater than that of $(\text{OC}_3\text{H}_7)_3\text{Al}$ [EtOH]. Therefore the concentration of $(\text{OC}_2\text{H}_5)_3\text{Al}$ ligands increases progressively after mixing. Since the resistance to hydrolysis increases with an increase in length of the alkyl group [EtOH], a slower hydrolysis is expected when the metal ligand is $(\text{OC}_3\text{H}_7)_3\text{Al}$ rather than $(\text{OC}_2\text{H}_5)_3\text{Al}$. When ethanol is used as a solvent, the metal ligand $(\text{OC}_2\text{H}_5)_3\text{Al}$ does not change, since the interchange of the ligand with the solvent yields the same product in the reactants. Consequently, hydrolysis is faster

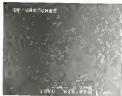


Figure 4-4. SEM micrograph of a surface film from HTLS and milk silica and hydrolysis time of 1 hour, fired at 1200°C.

where $(\text{OC}_2\text{H}_5)_2$ is the metal ligand due to the relative short length of the ethoxy group.

To investigate the possibility of performing hydrolysis after spinning, a sol was prepared without water. The sol was mixed with an alcohol sol and condensed to the proper viscosity for spinning. The fibers spun from the mixed sol were difficult to handle due to very low glass strength. This may show that the evolution of an interconnected polymeric structure prior to spinning is necessary to produce good quality films.

For all the methods used to prepare the multi sol, a prepolymer free and transparent sol was a prime consideration. The presence of prepolymers has a detrimental effect on the continuity of the fiber spinning process, since the prepolymers flocculate and plug the spinneret holes, impeding the spinning process. Prepolymers were formed when water was introduced along with triethanolamine (TEA) in the aluminum-*tert*-butoxide (AIB) solution, and when water was added to the multi sol.

It is believed that the formation of prepolymers is attributed to the rapid hydrolysis and condensation of AIB:



Rheology Study

Effect of Solvent Content and Condensation-Spinning Conditions

The rheological behavior of the molten sol as a function of solvent content was investigated. In addition, the rheological conditions for continuous spinning were determined. A variety of viscosity curves were obtained by evaporating solvent during the condensation step. Figure 4-5 shows plots of shear stress versus shear rate and viscosity versus shear rate for the molten sol EDOJ which had ethanol as solvent and THA as the chelating agent with a chelating agent/USP molar ratio (R) of 4.3. The three plots shown in Figure 4-5 correspond to three EDOJ sols with different amounts of solvent removed. The sol with high volume content of solvent exhibited Newtonian behavior (plot 1), in which the viscosity was shear rate independent. This behavior was due to the insignificant interaction between sol clusters.

When the solvent amount was decreased by condensation, the sol exhibited a shear thinning behavior (plot 2), in which the viscosity decreases with increasing shear rate (ScaFF). The decrease in the viscosity with the increase of shear rate can be attributed to the release of the condensed solvent within clusters after they break (ScaFF). Further condensation resulted in a sol with thixotropic behavior (plot 3). Thixotropic behavior occurs when a three-dimensional network is formed. This with-thixotropic behavior has an elastic character. After the yield stress is exceeded,

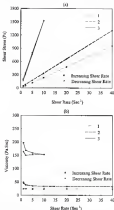


Figure 4-5. Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for ETL3 sol. Plot 1 corresponds to high solvent content, Plot 2 corresponds to medium solvent content and Plot 3 corresponds to low solvent content.

shear thinning behavior is accompanied by hysteresis [Barb7]. This behavior indicates that the broken network was not recovered when the shear rate was decreased.

It was observed that in order to achieve continuous spinning, slightly shear thinning behavior is required. The gel corresponding to plot (3) exhibited excellent spinnability. Also, the fibers spun from this gel had very good green strength. Gels with thixotropic behavior exhibited poor spinnability but reasonable green strength. On the other hand, gels with Newtonian behavior exhibited reasonable spinnability but broke into small pieces prior to drying. This poor green strength is due to the absence of a continuous structure. These results are also consistent with previous observations for silica gel [Barb7].

Change of Rheological Conditions with Time

The change of rheological behavior of modified gel spun at 4°C with aging time was studied. Figure 4-6 shows plots of shear stress versus shear rate and viscosity versus shear rate for EPLD gels immediately after condensation and 5 days after condensation. It was observed that the viscosity increased with time. However, the shear thinning behavior was maintained. Gels made with xanthanone [Xan6a] as a thickening agent with $R=0.13$ (labeled "EAD1P") exhibited a different behavior. Figure 4-7 shows that EAD 1P gels did not show a significant change in viscosity even after 18 days. However, a change was observed in the viscosity behavior and the gel became highly thixotropic after 18 days. This change in behavior may be attributed to the low R value used in the solution. Small R values generally result in a smaller

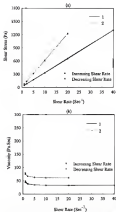


Figure 4-6. Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for PEG 200. Plot 1 measurement taken immediately after coordination, Plot 2 measurement taken 5 days after coordination.

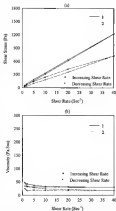


Figure 4-7: Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for E40 15 wt. Plot 1 measurement taken immediately after condensation, Plot 2 measurement taken 18 days after condensation

fraction of hydrolytic sites being blocked. As a result, hydrolysis and polycondensation can continue and lead to a three-dimensional network with anisotropic behavior.

Solvent Solvent Effect on Mullin Sol Rheology

The effect of silica sol solvent on mullin sol rheology was investigated. Figure 5-8 shows the rheological behavior of mullin sols with two different silica sol solvents, iso-butanol and ethanol. The mullin sol made with iso-butanol as silica sol solvent and TEA as chelating agent with $R=0.3$ was labeled "E00.3". This sol showed a Newtonian behavior, while E00.3, which used ethanol instead of iso-butanol as the silica sol solvent, exhibited shear thinning behavior. These results can be explained by considering the effect of silica sol solvent on the hydrolysis of TEOS that was presented in the preceding section. When iso-butanol was used, no significant hydrolysis was observed. As a result, structure evolution was very limited, and cluster interaction was minimal, which resulted in Newtonian behavior. On the other hand, when ethanol was used, hydrolysis was observed, and cluster growth took place as a result. The breaking of these structures and the release of the entrapped liquid resulted in the shear thinning behavior.

The Role of R Value

The effect of the molar ratio R on the sol rheological behavior was studied using acetylacetone and triethanolamine as chelating agents. When AcAc was used

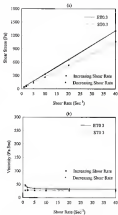


Figure 4-4 Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for ETR-2 and ETR-3 acids.

in the chelating agent, low values of R (<0.5) resulted in thixotropic sols which gelled readily when exposed to air. On the other hand, high values of R (>0.5) resulted in approximately Newtonian behavior. In addition, precipitate formation was observed in these sols. The optimum R value for maximum spreading and good stability of the sol was approximately 0.5. Figure 4-9 shows that the sol with $R=0.5$ (EAd-3) exhibits a slightly shear thinning behavior. The figure also shows that sols with $R=0.15$ (EAd-2) exhibit thixotropic behavior, and sol with $R=0.6$ (EAd-4) display Newtonian behavior. The thixotropic behavior was a result of the small fraction of hydrolysis sites blocked by the chelating agent, and the Newtonian behavior was a result of the large fraction of blocked hydrolysis sites.

When TBA was used as the chelating agent, similar results were observed. Figure 4-10 shows that for sol ET1, which had a $R=1$, Newtonian behavior was observed. No precipitate formation was detected in this sol. Sols with $R=0.5$ (ET3.5) exhibited a slightly shear thinning behavior, and possessed a very good spreading.

The effect R value has on the behavior of sols with different solvent contents was investigated. Figure 4-11 shows that EDC-3 sol exhibited a change in behavior from Newtonian to shear thinning upon condensation of the sol. Sols with $R=1$ (ET-2) on the other hand, did not show any change in the rheological behavior (from Newtonian/constant) upon condensation (Figure 4-11b). This result can be explained by considering the role played by the chelating agent. As mentioned previously, the chelating agent acts as a barrier toward the hydrolysis process by blocking hydrolysis

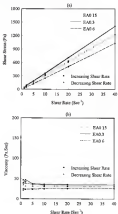


Figure 4-6 Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for EAB 15, EAB 3, and EAB 6 oils.

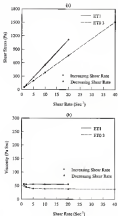


Figure 4-18. Flow of a) shear stress versus shear rate, b) viscosity versus shear rate for ETE3 and ETE1 sols.

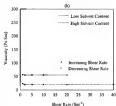
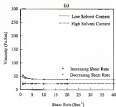


Figure 6-11. Plots for viscosity versus shear rate for a) ECD3.5 oil and b) ECD1 oil

the solvent content was decreased and cluster growth took place. When $R = 1$, the same. As R increases, the fraction of available hydrolysis sites decreases. The smaller the fraction of available hydrolysis sites, the more limited the growth of clusters. For the sets with a $R = 0.3$, the fraction of blocked hydrolysis sites was small. As a result, cluster growth was not restricted. Shear thinning behavior resulted when fraction of blocked hydrolysis sites was large. Consequently, cluster growth was restricted and the behavior remained Newtonian when the liquid content was decreased.

Thermal Analysis Study

Thermal analysis study was carried out using simultaneous TGA (thermal gravimetric analysis) and DTA (differential thermal analysis) analyses. Results of TGA/DTA analysis were used to determine the temperature range over which weight loss of films took place due to removal of organics and dehydrocyclization. In addition, DTA results were used to determine melting transformation temperature. Figure 6-13 shows TGA/DTA results for films from EPI-1 cut aged for 36 hours at room temperature. As shown in the figure, the weight loss comes at approximately 458°C . Melting transformation occurred at about 560°C , which is shown as the sharp endothermic peak. This melting transformation temperature is typical for single phase melting gels.

While chelating agents play a beneficial role in developing the desired rheological characteristics for fiber spinning, they induce other effects during

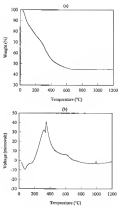


Figure 4-12. a) TGA and b) DTA results for E79.7 fibers aged for 24 hours at room temperature.

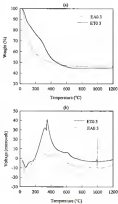


Figure 4-13. a) TGA and b) DTA results for EAB-3 and ETS-3 fibers aged for 24 hours at room temperature.

subsequent processing. Therefore, the effect of chelating agent on weight loss and mallic formation was investigated using TGA/DTA analysis. Figure 6-13a shows removal of organics was completed at lower temperatures with AcAc than with TEA. At 100°C, the E40.3 fibers had lost approximately 77% of the total weight loss, while the E70.3 fibers had lost only 41% of the total weight loss. Removal of organics and hydroxyl groups at low temperatures is important because it reduces the possibility of foaming and residual porosity due to gas entrapment. Foaming, or blooming, can occur if wetting takes place before the complete removal of volatile. Figure 6-14 shows blooming and the presence of porosity in E70.3 wet fibers that was heated quickly to 200°C without allowing organics to be removed.

The effect of the chelating agent on mallic transformation was also investigated. As shown in Figure 6-13b, both samples, E70.3 and E40.3, have mallic transformation peaks at approximately 90°C. However, the peak intensity is about 5 times larger in the case of AcAc (sample E40.3). These results indicate a significant enhancement in mallic formation when the AcAc is used. The enhancement in mallic formation may be attributed to more uniform mixing (on a molecular scale) achieved in sols prepared with AcAc.

Sol Preparation

Prior to fiber spinning, the sol is only partially hydrolyzed. Consequently, an aging step following spinning is of significant importance. The aging step aids in completing hydrolysis and polycondensation of the gel, and it can have an influence



Figure S-14 SEM micrograph for T03 fiber aged for 36 hours at room temperature and fired at 1500°C with heating rate of 15°C/min.

on the properties of the fired fiber. It was observed in this study that fibers that were not aged were soft, brittle, and very weak. These fibers retained a black color, indicative of the presence of residual carbon at temperatures as high as 1125°C.

Figure 6-13 shows the microstructure of a EAG3-60 fiber that was not aged. The presence of a significant porosity and irregular large grains is evident. The porosity can be attributed to the removal of volatiles at high temperatures rather than low temperatures (below sintering temperature). This can cause incomplete sintering. Figure 6-14 shows weight loss measured above 900°C for the unaged fibers. The presence of large irregular grains among small equiaxed grains may be attributed to the absence of molecular-scale homogeneity in the gel prior to crystallization. Aging can help in lowering the temperature of volatile removal. Figure 6-15 shows that while volatile removal for unaged fiber continued to above 1000°C, weight loss was ceased at about 600°C for aged fibers. Figure 6-17 shows the microstructure of EAG3-60 fiber aged at 100°C. The microstructure of the aged fiber does not show the presence of porosity. Also, a majority of the grains were small and equiaxed. No exaggerated grain growth, similar to that in the unaged fiber, was observed.

The role of aging time on sulfate formation was investigated. Figure 6-18 shows DTA results for ETL3-60 fibers with different aging treatments. For unaged fibers, the 590°C peak was not detectable. Fibers aged for 5 hours exhibited a small exothermic peak at temperature slightly above 590°C, and a larger peak was detected for fibers aged for 24 hours. Both samples were aged at more temperatures.

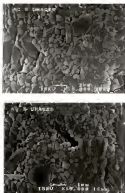


Figure 4-13: SEM micrographs for imaged EMI fiber fired at 1500°C for 30 min.

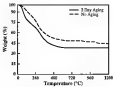


Figure 8-16. TGA results for aged and unaged E793 Siam.



Figure S-17 SEM micrograph of an E40.5 fiber aged at 100 °C with no hold time and observed at 150 °C for 10 min.



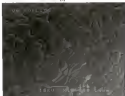
Figure 4-16. DTA results for ETAL3 films with different aging times.

These results indicate that longer aging times enhance melite formation. These results can also be explained in terms of fiber homogeneity. Absence of micro-scale homogeneity resulted in an undetectable melite transformation for the aged fibers because of the lack of local stoichiometry at the reaction temperature. The enhancement in the melite formation with increasing aging time can be attributed to the improvement in the micro-scale homogeneity. This improvement in homogeneity is a direct result of hydrolysis and polycondensation reactions taking place during aging.

The role of aging temperature on fiber microstructure was studied. It was observed that aging temperature had an important effect on fiber grain size. High aging temperatures produced smaller grain sizes. Figure 4-15 shows the microstructure of room temperature aged ETL3 sol fibers (24 hr aging time), and the microstructure of the same fibers aged at 100°C (with no hold time). A significant difference in the grain size was observed. Similar microstructure was observed for EAL3 sol fibers aged at 100°C (Figure 4-16). Fibers from EAL3 sol aged at 80°C showed a significantly larger grain size (Figure 4-17).

Upon examination of both types of fibers aged at 100°C, the EAL3 fibers (that were made with Acetic as the chelating agent) were found to be strong and flexible, while ETL3 sol fibers (that were made with TEA as the chelating agent) were weak and brittle. Density of the ETL3 fibers was 1.7 g/cm³ while the density of EAL3 fibers was 3.1 g/cm³. Examination of ETL3 fiber ends showed a significant separation between an outside tubular shell and an inside fiber core.

(a)



(b)



Figure 6-19. SEM micrographs of PZL3 films: (a) aged at room temperature for 10 hours (b) aged at 100°C with no hold time. Both films were clustered at 1500°C for 10 min.



Figure 8-28 SEM micrograph of an E463 fiber aged at 150 °C with no hold time and annealed at 1500 °C for 10 min.

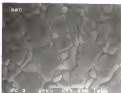


Figure S-20. SEM micrograph of an OLS film aged at 40°C with no hold time and annealed at 150°C for 15 min.

(Figure 4-12). The structure resulted in the poor mechanical properties of these fibers. Figure 4-23 shows a uniform microstructure across the fiber and the absence of large pores in EAO3 fibers.

These results can be attributed to the difference in the aging (hydrolysis and polycondensation) rate between the two fibers. Fibers made with AcAc as a chelating agent complete aging faster than fibers made with TEA. The variance in the extent of aging across the fiber in the case of ETD3 fibers resulted in a dense outside shell and a porous inside core. In contrast, EAO3 fibers did not show a difference in the microstructure across the fiber, since no significant variations in aging existed. These results indicate that AcAc is a better choice of chelating agents if high temperature aging is to be used.

Maintaining a constant aging temperature, the effect of R value on grain size was investigated. Fibers from soils EAO3 and EAO6 (corresponding to R=0.5 and R=0.6, respectively) were aged at 80° C and fired at 1500° C. A comparison between Figures 4-25 and 4-26 show that EAO3 fibers had a significantly larger grain size than EAO6 fibers. The small grain size of the EAO6 fibers was a result of the chelating agent's effect on hydrolysis. High R values resulted in smaller fraction of hydrolysis sites, and consequently, a smaller fraction of polycondensation sites. The small fraction of polycondensation sites restricted cluster growth in the sol. As a result, small grains were produced upon firing.

High temperature aging has the following advantages when used in processing of EAO3 fibers:



Figure 4.22 SEM micrograph of ETL3 fibers aged at 100°C with no-fold case and annealed at 150°C for 10 min.

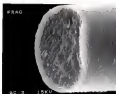


Figure 4-23 SEM micrograph of an EAO3 fiber aged at 300°C with no hold time removed at 1500°C for 10 min.

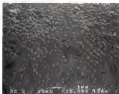


Figure 4-34 SEM micrograph of an E40 steel specimen heat treated at 1500°C with no hold time and cooled at 1500°C for 10 min.

- improved reaction kinetics, and as a result, aging time can be reduced. This point is crucial when considering a continuous spinning process.
- improved macro-scale homogeneity, and as a result, fibers are produced with relatively small grain size. Small grain size fibers are desirable when achieving high strength is required.

Densification Study

Apparent density measurements were carried out for the EA63 and ETL3 fibers aged at room temperature for 24 hours and fired at different temperatures with a heating rate of 10°C/min. Figure 4-25 shows the densification behavior for both types of molten fibers. The error bars were not shown in the figure due to the very small values of the standard deviation ($\sigma = 0.0017\%$). At temperatures below 800°C, EA63 fibers had lower density than ETL3. This may be a result of the removal of organics at a lower temperature as was the case for EA63 fibers, as discussed earlier.

Significant increase in the density occurred in both samples above 800°C due to viscous flow sintering. The sintering rate was faster for the EA63 fibers. At a temperature of 1000°C, EA63 reached about 90% of its final density, while the ETL3 fibers reached approximately 80% of final density. Figures 4-26 and 4-27 show polished sections of EA63 and ETL3 fibers fired at 1000°C. Some porosity was observed in the ETL3 fibers, but none was observed in the EA63 fibers. Figure 4-28 shows an unpolished section of ETL3 fiber with large porous points.

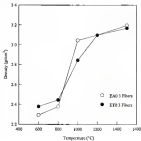


Figure 6-25: Densification curves for EAO-5 and ETV-3 fibers aged for 28 hours at four temperatures.

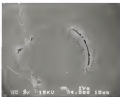


Figure 4-25. SEM micrograph for a polished cross section of SiO₂ fiber annealed at 1500°C for 10 min.

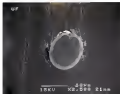


Figure 4-27 SEM micrograph for a polished cross section of ETEJ fiber sintered at 1500°C for 10 min

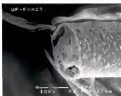


Figure 4-18 SEM micrograph of an SiTC-3 fiber sintered at 1500°C for 10 min.

It was observed that the final apparent density depends on aging temperature. Fibers aged at 50°C and 100°C had apparent densities of 2.9 and 3.2 g/cm³, respectively after annealing at 1500°C for 10 min. This change in density with aging temperature is attributed to the extent of aging reached at a certain temperature. The higher the aging temperature, the higher the vapor pressure. Also, aging reaction kinetics are enhanced at high temperatures. Therefore, high aging temperatures produce fibers with less organic content, and consequently, less organic material was removed during firing providing higher densities.

Crystalline Phase Determination

Crystalline phase determination was carried out using x-ray diffraction (XRD). The XRD pattern for pure mullite powder shown in Figure 4-29 was used as a reference to determine if mullite was the only phase formed in the fibers. Fibers from E44.3 and ET4.3 sol were fired at 1000°C, which is slightly above the maximum observed in the DTA curve. Both samples showed patterns (Figure 4-30 and 4-31) identical to the pure mullite pattern shown in Figure 4-29. Fibers from the same sols were fired at 1500°C and showed patterns identical to the ones in Figures 4-30 and 4-31. These results show that there was no phase transformation above 1000°C from another crystalline phase to mullite. The results indicate that the 850°C exotherm corresponds to mullite formation, and that mullite was the only crystalline phase present. The positions of XRD peaks and their intensities for ET4.3 fibers fired at 1500°C, for pure mullite powder, and for the standard ASTM peaks are presented in Tables 4-1, 4-2, and 4-3. The results shown in Tables 4-1 and 4-2 indicate that

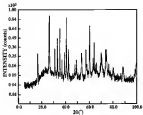


Figure 4-29 XRD pattern for pure malite powder

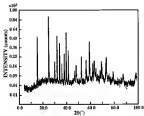


Figure S-38. XRD pattern for B433 fibers fired at 1000°C.

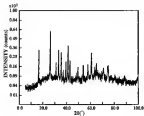


Figure S-31. XRD pattern for ETX3 film heat treated at 1000°C.

Table 4-1. Positions of XRD peaks and their intensities for ETR-5 fibers

Peak Number	Angle (Degree)	Intensity (%)
1	8.045	2.28
2	16.443	24.04
3	26.005	61.58
4	26.305	95.99
5	30.035	31.67
6	33.253	34.89
7	35.800	74.26
8	39.683	17.39
9	39.323	30.32
10	40.900	100.00
11	42.678	37.87
12	48.143	19.23
13	48.463	17.73
14	50.483	13.41
15	51.948	22.86
16	57.625	34.32
17	58.373	9.87

Table 4-1: Positions of XRD peaks and their intensities for pure melittite powder

Peak Number	Angle (Degree)	Intensity (%)
1	16.498	20.96
2	26.025	82.08
3	26.353	53.35
4	31.073	20.34
5	33.306	52.64
6	33.348	73.42
7	37.095	34.05
8	39.328	28.59
9	40.953	100.00
10	43.676	24.84
11	46.339	10.76
12	49.553	17.73
13	53.546	17.10
14	59.933	20.90
15	57.643	35.26
16	59.813	13.30

Table 4-3 Positions of XRD peaks and their intensities for the standard ASTM peaks.

Peak Number	Angle (Degree)	Intensity (%)
1	16.402	50
2	25.594	8
3	25.971	95
4	26.267	100
5	30.960	30
6	33.228	40
7	35.278	30
8	36.493	14
9	38.952	4
10	39.276	30
11	40.174	40
12	42.390	25
13	42.808	8
14	46.049	2
15	47.217	2
16	48.154	8
17	49.468	18
18	53.462	6
19	53.853	14
20	54.000	18
21	57.261	28
22	58.412	12

molten fiber peaks match all molten powder peaks with very small difference in peak position (maximum difference in peak position = 0.05°). Comparing Table 4-3 to Table 4-1, all peaks with intensity > 10 in the ASTM file matched the molten fiber peaks with very small difference in peak position (maximum difference in peak position = 0.05°).

Glass Phase Detection

The presence of an intergranular glass phase in molten fibers can result in detrimental effects on high temperature properties of the fibers. The intergranular glass phase causes a deterioration in the creep resistance of the fibers, this limits their use at high temperatures. Since the main application for molten fibers is at high temperatures, production of glass-free molten fibers is crucial.

Two techniques were used for glass phase examination, chemical etching and transmission electron microscopy (TEM). The chemical etching technique is based on the large difference in the dissolution rate of the siliceous glass phase and molten α -hydrofluoric acid (HF). The glass phase dissolves readily in HF while molten has a very low dissolution rate [Sar79]. The chemical etching experiments were carried out by immersing fibers in 50% HF solution for 15 minutes. Micrographs were taken using SEM before and after the etching treatment to determine if there were differences at the microstructure. Fibers produced by the processes developed in this study were anticipated to consistently produce molten fibers.

Figures 4-32a,b and 4-33a,b show ETEC and Nasco 480 fibers before etching at different magnifications. Figures 4-34a,b and 4-35a,b show the fibers after the

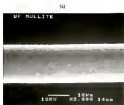


Figure 4-3. SEM micrograph of an EPO fiber before picking up at 3000X and b) at 15000X

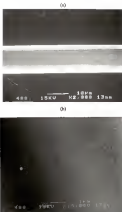


Figure 4-10 SEM micrographs for a Naval 440 steel before etching a) at 2000X and b) at 10000X.

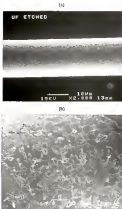


Figure 6-14 SEM micrograph for an etched BTGA film up at 3000X and 15) at 15000X.

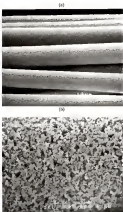


Figure 4-35 SEM micrograph for etched Nexel 445 fibers a) at 20000x and b) 40000x.

etching treatment. No detectable difference was observed in the microstructure of E70.3 fibers after etching, indicating that there was no significant amount of glass phase present. In contrast, Nexcel 400 fibers exhibited a significant difference in the microstructure after etching. The etched Nexcel 400 fibers showed a network of porosity that resulted from the dissolution of the glass phase. These results indicate that Nexcel 400 fibers contain a large amount of glass phase. Figure 6-36 shows the microstructure of an etched Alcoa fiber produced by Sarnasene company. Alcoa fibers contain 10 wt% silica and 10 wt% alumina. Although the Sarnasene fiber composition has a lower silica content than the fibers produced in this study, the etching treatment resulted in the dissolution of an intergranular glass phase, as shown in Figure 6-36. Results for E-40.2 fibers were similar to those obtained for E70.3 fibers. Figure 6-37 indicates that there was no detectable amount of glass phase present in these fibers.

Micrographs taken by TEM confirmed the results achieved by chemical etching for E70.3 fibers. Figures 6-38 and 6-39 show that no glass phase was present at the grain boundaries or at the triple junction points. Fibers made with sec-butanol as the silica solvent (E71.3 wt) which, as mentioned previously, had a poor homogeneity, showed the presence of an intergranular glass phase (Figure 6-40). It was observed in this study that the absence of molecular-scale homogeneity of the gel may lead to the presence of an intergranular glass phase.



Figure 6-36 SEM micrograph of an etched AlGaAs film at 150,000X.

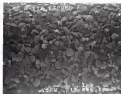


Figure 4-21. SEM micrograph of an etched BAQ3 fiber at 1000X.



Figure 6.26. TEM micrograph of an EPO-S fiber at 200,000X. Samples were prepared and micrographs were taken by A. Maccione.

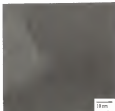


Figure 4-18. TEM micrograph of an ETL3 fiber at 150,000X. Samples were prepared and micrographs were taken by A. Mirrezaei.

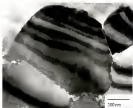


Figure S-40 TEM micrograph of STech fibers at 100,000X. Samples were prepared and micrographs were taken by A. Mhanna.

Grain Growth Study

Grain growth can result in detrimental effects on fiber strength if large grains are produced. The strength of polycrystalline materials is inversely proportional to the grain size (Kao²⁹). Since melting fibers are primarily used at high temperatures, grain growth is expected due to the strong dependency of grain growth on temperature. The grain growth follows the Arrhenius equation (Kao²⁹).

$$G = G_0 \exp\left(-\frac{Q}{kT}\right) \quad (4.4)$$

where G = growth rate, G_0 = constant, Q = activation energy for grain growth, k = Boltzmann constant, T = temperature.

The change in the grain size as a function of temperature and time was examined. The grain size was measured using SEM. To examine the grain growth as a function of temperature, EAA3 fibers (pre-annealed at 1500°C) were annealed at different temperatures, but with constant annealing time (1 hour). The results are presented in Figure 4-41. The figure shows that up to 1400°C, there was no measurable increase in grain size for 1 hour hold period. However, a significant increase in the grain size was observed at 1500°C.

The grain growth as a function of time was investigated using EAA3 fibers (pre-annealed at 1500°C). The fibers were annealed at 1700°C for different periods of time. Figures 4-42 and 4-43 show the change in the grain size with annealing time at 1300°C and 1400°C. No significant change in the grain size was observed over

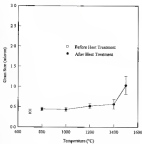


Figure 4-41. Glass transition temperature increasing temperature for EACB fibers (pre-treated at 2500°C) with 1 hour annealing time

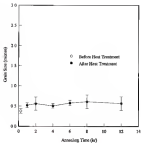


Figure 4-42 Grain size versus annealing time for EAGS fibers (pre-annealed at 1500°C) with annealing temperatures of 1500°C.

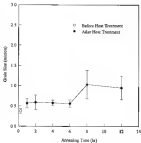


Figure 4-45. Circle size versus annealing time for E-63 film (presterilized at 170°C) with annealing temperature of 140°C.

for annealing times as long as 12 hours at 1300°C. However, for annealing temperatures of 1400°C, grain growth was observed after annealing times of 4 hours. These results show that the process for grain growth has a high activation energy so that time-dependent growth is not observed at temperatures up to 1300°C. A significant change occurs in 1 hour at 1300°C or in 4 hours at 1400°C.

Tensile Strength Measurements

The tensile strength of ETEJ and EAJJ fibers was measured. Both types of fibers were annealed at 1400°C. However, ETEJ fibers were aged for 24 hours at room temperature, while EAJJ fibers were aged at 100°C with no hold time. Many of the ETEJ and EAJJ fibers failed near the area where the glue was applied. No strength values were reported for these fibers as the results were not representative of the tensile strength of the fiber. Results are reported only for fibers that failed at regions other than the glue interface.

The tensile strength of fibers was calculated by the equation

$$\sigma_T = \frac{F}{r^2 \lambda_m} \quad 8.3$$

where σ_T = tensile strength, F = applied tension force at fracture, and r = fiber radius. Fiber diameters were 15-25 microns for ETEJ fibers and 15-20 microns for EAJJ fibers.

The measured tensile strengths for the two types of fibers were as follows:

- For ETL3 fibers: $\sigma_T = 0.26$ GPa

number of samples = 27

number of samples that broke at the middle
during testing = 5

standard deviation = 0.05

- For EAA3 fibers: $\sigma_T = 0.44$ GPa

number of samples = 26

number of samples that broke at the middle
during testing = 3

standard deviation = 0.03

Only the samples that broke in the middle were taken into account in measuring the fiber strength and the standard deviation. The difference in the tensile strength can be attributed to the difference in grain size and porosity. The average grain size of ETL3 fibers was about 1.15 μm , while the average grain size for EAA3 fibers was 0.27 μm . Also, it was shown in a previous section that ETL3 fibers exhibited some porosity due to the high temperature required for separation removal. The EAA3 fibers did not exhibit porosity. Preliminary measurements on EAA3 fibers sintered at 1200°C yielded tensile strength data as high as 1.15 GPa. This is presumed to result from an even smaller grain size.

Comparison Study

In this section, the results achieved in this study are compared to the results reported previously in the area of sol-gel processing of molten as well as processing of molten fibers. It was shown in this study that there was a single phase transformation that occurred at 850°C to form molten. Some previous studies showed more than one phase transformation before forming molten

- Prochaska and King results showed a phase transformation at 850°C to form γ - Al_2O_3 or spinel, and another phase transformation at 1280°C to form molten (Proch⁸⁷)
- Peak and co-workers results showed a phase transformation at 1400°C to spinel followed by transformation to molten at 1200°C (Peak⁸⁷)
- Richards and co-workers results indicated a phase transformation at 870°C to spinel, followed by transformation to molten at 1293°C (Rich⁸⁷)

One of the main objectives of this study was to produce single phase molten fibers with no intergranular glass phase. Results indicate this objective was achieved.

However, other studies reported the presence of more than one phase:

- Peak and Jemel showed the presence of a glass phase (Peak⁸⁷,Jemel⁸⁷)
- Helling and Masing showed the presence of intergranular molten and glass phases (Hell⁸⁸)
- Wei and Hsichon showed that molten produced contained chlorine particles (Wei⁸⁸)

- Schneider and co-workers indicated the formation of $\gamma\text{-Al}_2\text{O}_3$ microtubules and nodules in the system they studied [Sch62].
- Somparjak showed the presence of spiral and glass phase [Som64].
- Tests of commercial Nural fibers conducted in this study showed an appreciable glass phase.

Production of fibers with squared grains was achieved in this study. Previous studies carried out by Hirai and Laughon and Lu and Thomson produced circular grains [Hir66, Lu74, and Kim53]. The grain size of fibers produced in this study (K400.3 fibers) was 0.37 microns compared to the 2-4 micron grain size produced by Todda and Pandey [Tod68].

Venkatesh and co-workers was able to produce single phase nodule fibers with small squared grains. However, these fibers were short because continuous spinnability could not be achieved [Ven68]. In this study, continuous spinning of fibers was achieved. Taylor and co-workers were able to produce nodule fibers. However, fiber diameters were large (118 microns), the fibers were brittle, exhibited porosity and microvoids [Tau55]. Fibers produced in this study (K400.3) had small diameter (10-20 microns). These fibers were flexible and did not have porosity or microvoids. Nodule fibers produced by Kim and co-workers had needle-like grains compared to squared grains achieved in this study [Kim53]. No reference for grain size, fiber diameter, or fiber strength was found in Kim's work. Also, the presence of an intergranular glass phase was not investigated.

CHAPTER 7 SUMMARY, CONCLUSIONS AND FUTURE WORK

A process was developed to produce continuous molten fibres. The conditions to achieve continuous spinnability and the factors that affect the rheological behavior of molten sol were determined. The optimum value for chelating agent/alanine precursor molar ratio was determined. Also, the effects of changing the chelating agent on organics removal, molten formation, fiber aging, fiber densification, and fiber microstructure were investigated. The role of aging in molten transformation and its effect on the properties and microstructure of fibers were determined. In addition, the effect of aging temperature on properties and microstructure was obtained. The fibers were tested to determine if there was an intergranular glass phase and was compared to commercial molten fibers. The grain growth was determined as a function of time and temperature.

Conclusions

The following conclusions were drawn from the work done during the study:

- The conditions for continuous spinnability of molten sol were determined. Continuous spinnability was achieved when the sol flow behavior was slightly shear thinning;
- Sol viscosity increased significantly with time but flow behavior remained

the same for sols with moderate values of R ($R=6.3$). For low values of R ($R<6.3$), viscosity did not change significantly, but flow behavior was altered.

- Shear thinning behavior was observed when silica hydrolysis occurred, and Newtonian behavior was observed when silica hydrolysis did not occur.

- Bots with low R values exhibited thixotropic behavior, while those with intermediate and high R values exhibited shear thinning and Newtonian behavior, respectively.

- Change of solvent content resulted in a change in flow behavior for sols with moderate R values ($R=6.3$), but it did not result in a change in behavior for sols with high R values ($R>10$).

- Pre-spraying/hydrolysis of silica sol was important to achieve good strength for green fibers and good microstructure for sintered fibers. Also, pre-spraying hydrolysis of silica sol aided in avoiding the formation of an intergranular glass phase.

- Lower temperatures of sintering were required and significantly enhanced molten transformations were achieved when AcAc was used as a sintering agent.

- Fiber aging was shown to be crucial in attaining quality fibers. Un-aged fibers showed significant porosity and large irregular grains, while aged fibers did not show the presence of porosity and the grains were agglomerated and small.

- Aging resulted in enhancing molite formation.

- The grain size increased with increasing aging temperature.

- Fiber density increased with increasing aging temperature.

- Fibers made with AcAc spun more efficiently at high temperatures than those made with TEA.
- The densification rate was higher for fibers made with AcAc than those made with TEA.
- Melite was the only crystalline phase present above 1000°C.
- Neither fibers made with TEA nor fibers made with AcAc showed the presence of an intergranular glass phase.
- Intergranular glass phase was present when pre-spinning hydrolysis of silice was not accomplished.
- Commercial melite fibers showed the presence of intergranular glass phase.
- Grain growth was not significant for temperatures up to 1400°C.
- Grain growth was not significant for periods as long as 12 hours at 1200°C.

Future Work

Although extensive research has been conducted on the processing of melite fibers, additional research is proposed in several areas. These include:

- Evaluate different techniques to inhibit grain growth in melite fibers.
- Investigate the possibility of using the microwave energy in processing of melite fibers. The study could include:
 - measure the dielectric properties of fibers at different temperatures,
 - design microwave ovens for the different processing steps (i.e., organic removal, dehydration and sintering).

- study the change in reaction kinetics compared to conventional heating, and
- analyze the effect of microwave on drying and organic removal, coloring, malic transformation, and grain growth.

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BIOGRAPHICAL SKETCH

Salwan Al Azzawi was born in Baghdad on November 14, 1965. He was raised in Hay Al-Adil on the western side of Baghdad. In 1983 he was admitted to the University of Mosul and majored in mechanical engineering. In 1984 he transferred to the University of Baghdad where he continued his studies in mechanical engineering. In 1988 Salwan was selected to continue his education in the Department of Nuclear Engineering. He completed his undergraduate studies in 1988, receiving a bachelor of science degree in nuclear engineering. In 1989 he was awarded a government scholarship to continue his graduate education in the United States. He was admitted to the University of Florida in May of 1989 where he joined Dr. Clark's ceramic processing group. His research focused on the microwave sintering of ceramic composites with alumina glass and he was awarded his Master of Science degree in May, 1993. Salwan joined Dr. Simmons' research group in 1992 where his studies focused on processing of continuous ceramic fibers prepared using sol-gel techniques. He is a member of the American Ceramic Society, the National Institute of Ceramic Engineers and Keratists, the ceramic engineering honor society. His hobbies include basketball, tennis, bowling and travel.

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